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THE THERMODYNAMIC PROPERTIES OF
NITROGEN - OXYGEN MIXTURES

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DATE: 17 MAY 1968

Thesis
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THE THERMODYNAMIC PROPERTIES OF
NITROGEN-OXYGEN MIXTURES

by

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(1960)

Submitted in Partial Fulfillment of the
Requirements for the Degree of
Naval Engineer and the Degree of
Master of Science in
Mechanical Engineering
at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

May, 1968

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ABSTRACT

Title: The Thermodynamic Properties of Nitrogen-Oxygen Mixtures

Author: LT Robert L. Steele

Submitted on May 17, 1968 to the Department of Mechanical Engineering in partial fulfillment of the requirements for the Master of Science degree in Mechanical Engineering and to the Department of Naval Architecture and Marine Engineering in partial fulfillment of the requirements for the Professional Degree, Naval Engineer.

This thesis includes a survey of the literature through 1967 on the methods of determination of the thermodynamic properties of nitrogen-oxygen mixtures in the two-phase, liquid-vapor region. The virial expansion, empirical equations of state, pseudocritical constants, excess functions, latent heats, and graphical methods are considered.

The methods just enumerated are evaluated for their simplicity, feasibility, and accuracy. On the basis of the state of the art and the availability of appropriate data, thermodynamic diagrams are constructed for 1, 5, 10 and 20 atmospheres of pressure in the two-phase region. Diagram coordinates are enthalpy-composition and entropy-composition. The diagrams at atmospheric pressure show good correlation with known data, while those at higher pressures are best estimates using excess functions and idealizing assumptions.

Thesis Supervisor: J.L. Smith, Jr.

Title: Associate Professor of Mechanical Engineering

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LIST OF SYMBOLS

- $a, b; a_m^*, b_m^*; a_i^*, b_i^*$ --- single substance, mixture and pure component of mixture constants in Redlich-Kwong eqn. of state.
- a, A, b, B, c, C --- constants in Barker's expression for G^E .
- $B(T), C(T)$ --- 2nd & 3rd virial coefficients for a single substance.
- $B_{ij}, B(T,x), B_m$ --- 2nd & 3rd virial coefficients for a mixture.
- $C_{ijk}, C(T,x), C_m$
- $B_{AA}, B_{BB}, C_{AAA}, C_{BBB}$ --- 2nd & 3rd virial coefficients for pure components in a binary mixture.
- B_{AB}, C_{ABB}, C_{AAB} --- 2nd & 3rd interaction or cross virial coefficients for a binary mixture.
- $B^*(T), C^*(T)$ --- 2nd & 3rd universal, single substance, virial coefficients.
- b_o --- "hard sphere" molecular volume $= (2/3)\pi N_o \sigma^3$
- C_p^o --- specific heat at constant pressure for perfect gas or at zero pressure.
- $D(T,x)$ etc. --- 4th virial coefficient.
- E --- internal energy.
- f --- fugacity of a single substance.
- \bar{f}_i --- fugacity of component i in solution
- f_i --- fugacity of pure component i at same T, P of the mixture.
- G --- Gibbs free energy $= H - TS$.
- H --- enthalpy $= E + PV$
- $\Delta H_{lv}, \Delta H_{vl}$ --- differential heat of vaporization and condensation at constant temperature.
- j --- absolute joules
- k --- Boltzmann constant $= 1.38054 \times 10^{-23} \text{ J/oK}$
- L, M, N --- defined by Eq. (58).
- n --- number of moles.

P --- pressure.

P_i --- pure-component pressure of component i in a gas mixture.

\bar{P}_i --- partial pressure of component i in ideal gas mixture,

$$\bar{P}_i = x_i^l P \text{ (Dalton's Law).}$$

R --- universal gas constant = 0.0820535 liter atm/mole $^{\circ}\text{K}$

R --- any extensive property

\bar{R}_i --- partial property of component i in solution.

S --- entropy

T --- absolute temperature.

T_0 --- base or reference temperature.

U --- intermolecular interaction energy.

V --- molal or specific volume

\bar{V}_i --- partial molal volume of component i in solution.

x_i --- mole fraction of a component i in a mixture = n_i/n .

Z --- compressibility factor = PV/RT

superscripts

E --- excess property.

l --- property of the liquid phase; property of the liquid line.

v --- property of the vapor phase; property of the vapor line.

m --- property of mixing.

o --- zero pressure state or perfect gas state at any pressure.

subscripts

b --- refers to the normal boiling point.

i --- pure component property of a mixture.

m --- property of a mixture.

c --- critical property.

cm --- pseudocritical property.

r --- reduced state.

s --- reference state.

Greek symbols

α --- volatility ratio.

γ --- activity coefficient.

θ --- general function of temperature.

ϵ --- characteristic molecular energy.

σ --- characteristic molecular distance.

Δ --- finite change of quantity.

μ --- chemical potential = \bar{G}

All state properties are given in their molal or specific property form unless otherwise noted.

INTRODUCTION

It is the purpose of this thesis to present the results of a search of the literature and the subsequent analysis of the findings of that search. The subject of the inquiry was the thermodynamic properties of nitrogen-oxygen mixtures in the two-phase, liquid-vapor region. The reasons for the study of the elemental properties of any basic substances are self-evident especially for substances as fundamentally important as the mixtures of nitrogen and oxygen. It should suffice to say that the hunt carried the author through the fields of cryogenics, low temperature physics, high pressure physics, thermodynamics, physical chemistry, molecular chemistry and statistical mechanics. It is the intent of this thesis to extract from these areas of science and engineering the most appropriate analytical, graphical and machine methods of determination now available and to present the properties determined therefrom.

Acknowledgement and appreciation are expressed for the aid, assistance, and direction of Professor J.L. Smith, Jr. of the MIT Cryogenics Laboratory.

PROCEDURE

The direction of this work consisted of two distinct phases. The first part of the effort was directed toward a thorough search of the scientific and engineering literature. This was accomplished by a personal search of the Chemical Abstracts through 1967. Machine programmed searches were conducted for the author by the Cryogenics Engineering Laboratory of the National Bureau of Standards and the Defense Documentation Center. These initial efforts were principally centered on nitrogen-oxygen mixtures and the thermodynamic approaches to the derivation of properties of binary mixtures. As the work progressed, molecular theory became of interest, and the extensive bibliographies in the major texts of the field were utilized. At the end of each subsection of the Results, the references are listed which deal explicitly with that subsection as annotated in the text.

The second part of the program was the analysis of the data which had been found. It must be said that the determination of the properties of a mixture would be a relatively easy problem if the mixture behaved simply as the average of its constituents. Unfortunately, not only are the constituents themselves not ideal, but also they interact with each other in a non-ideal manner.

It is intended in this thesis to discuss the PVT behavior of mixtures and the various methods of deriving their thermodynamic properties: enthalpy and entropy. Specifically the next section will cover the following:

- a. the theory of corresponding states and pseudocritical constants.

- b. empirical equations of state.
- c. the virial expansion.
- d. partial property correlations and mole fraction averaging.
- e. excess functions as deviations from ideality.
- f. graphical derivations.
- g. latent heat techniques.

No attempt has been made to make interpretations based on statistical mechanics and its application to molecular theory. The reader interested in approaches based on this field must consult the works of Eyring, Kirkwood, Lewinson, Hirschfelder et al for their treatment on the formal and model approaches in this area.

The final section of the Results will correlate the discussed data and provide a graphical presentation of the enthalpy and entropy of binary mixtures of nitrogen and oxygen at various pressures.

RESULTS

Phase Equilibria

Perhaps the information most consistently required in calculations concerning the two-phase region is the equilibrium behavior of the system as defined by Gibbs [1]. The study of vapor-liquid equilibrium would obviously be simplified if the phases behaved as ideal solutions, for then we should only require information about the pure components in order to develop values for the mixtures.

Deviations from ideal behavior occur in both the liquid and the vapor phases as a result of the forces that exist between the molecules. The magnitude of the intermolecular forces depends on the nature of the molecules and the average distance between them as expressed by

$$U_{AB}(r)/\epsilon_{AB} = f(r/\sigma_{ab}) \quad (1)$$

This expression of the principle of corresponding states [2,3] says that the interaction energy of a pair of molecules A and B at a distance r apart may be expressed in terms of a universal function f for all A and B. The parameters ϵ_{AB} and σ_{AB} are a characteristic energy and distance respectively for the pair of molecules. In the liquid state the molecules are relatively close together, and the force fields are strong, so that differences in shape and charge distribution will cause deviations in behavior. In the gas phase the force fields are not as strong, and at low pressures ideal mixture behavior is a good approximation. Note that a perfect gas is defined in terms of negligible

forces between molecules, whereas an ideal mixture or solution requires only the same forces between like and unlike molecules. Hence, at low pressures ideal solution deviations are principally due to the liquid phase while at high pressures both vapor and liquid phases contribute.

It is perhaps instructive to review the phase behavior of mixtures under pressure [4,5,6]. In Fig. 1 the curves OC_{N_2} and OC_{O_2} represent the usual vapor pressure curves for the pure components terminating at their respective critical points. For the binary system, however, the phase boundary is the region enclosed

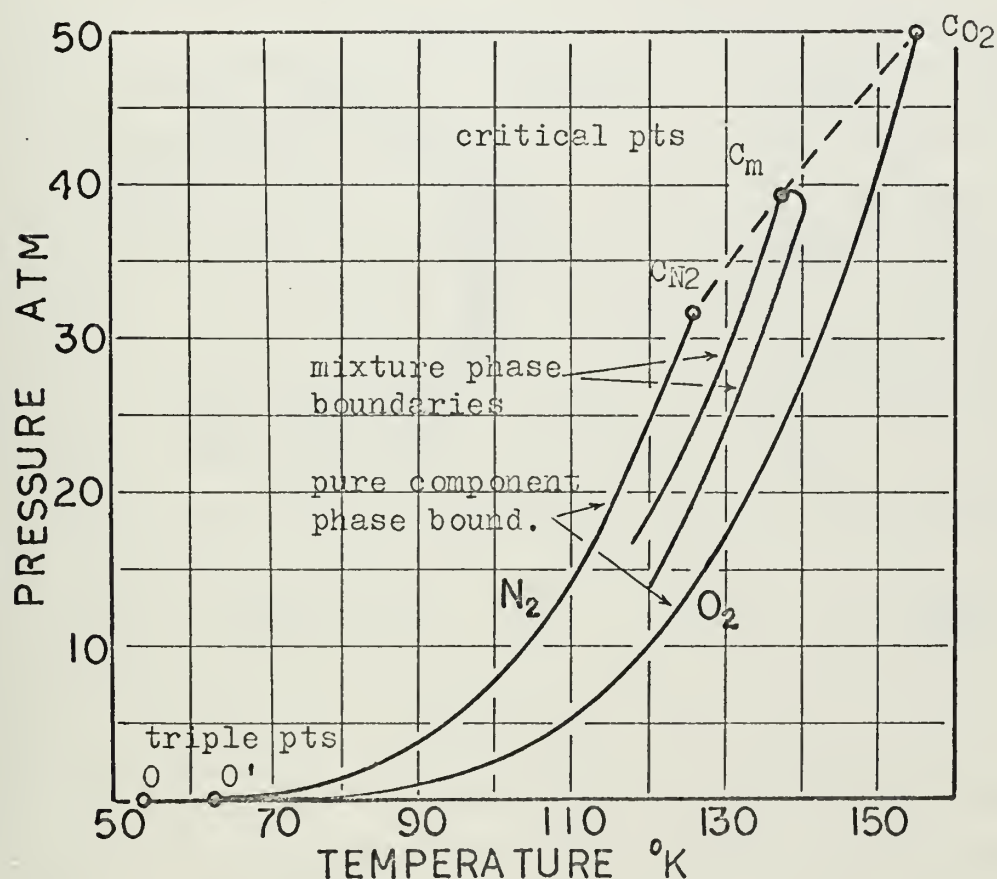


Figure 1. Phase boundaries of pure components and mixtures.

by the curve OC_mO' within which both the liquid and the vapor coexist. The critical point of the mixture, C_m , is defined as the state at which the properties of the vapor and liquid phases in equilibrium are identical. If the phase boundary curves of several mixtures of different compositions are drawn, the locus of their critical points form an envelope indicated by the dashed line in Fig. 1. The maximum pressure and temperature for the existence of two phases are called the cricondenbar, C_p , and the cricondentherm, C_T , respectively [7]. These are illustrated in Fig. 2 as is the phenomena of retrograde condensation 8 .

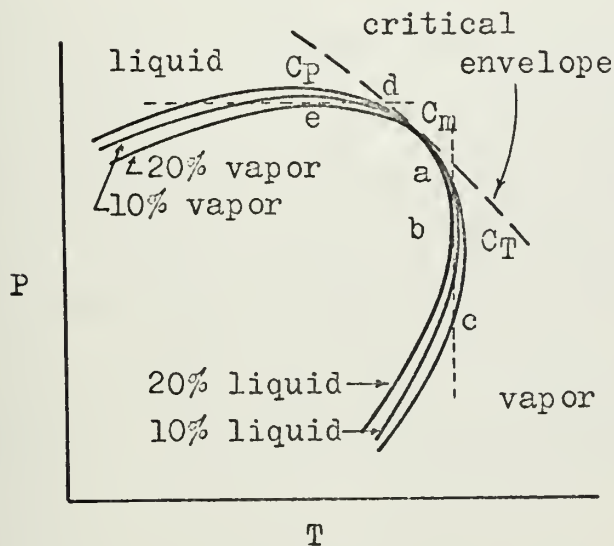


Figure 2

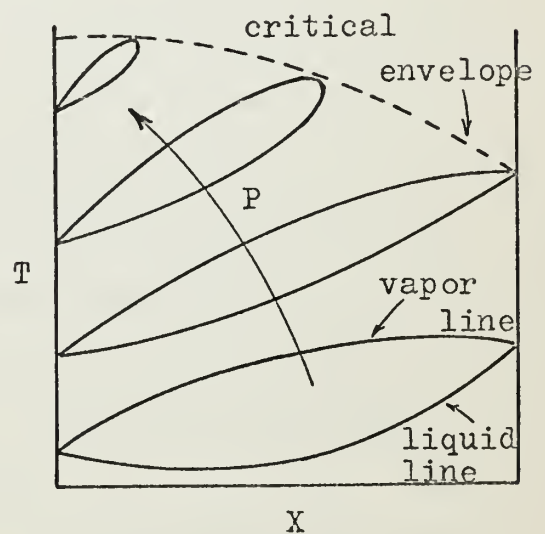


Figure 3

In Fig. 2 it can be seen that if a line of constant temperature is followed, condensation will begin at point a and will continue with decreasing pressure until maximum condensation is reached at point b, at which time vaporization will occur until the system is again all vapor at point c. A similar phenomena will take place at constant pressure with vaporization occurring with decreasing

temperature from points d to e.

The diagrams most frequently used in representing equilibrium data are those of pressure or temperature as a function of molar composition. Fig. 3 shows the trend of the phase boundary curve with increasing pressure when the mixture critical temperature and pressure fall between those of the pure components. The area of two-phase coexistence decreases with increasing pressure. The phase boundary curve breaks away from the pure component whose critical temperature is lowest and recedes along the critical envelope, finally disappearing altogether at the higher critical point.

Turning to nitrogen-oxygen mixtures in particular, the earliest investigation of their equilibria was conducted by Baly in 1900 at atmospheric pressure [9]. The temperature scale used by him was in error, and his vapor composition measurements proved to be innaccurate. Inglis [10] in 1906 made measurements at 74.7 and 79.07°K resulting in vapor pressures between 1 and 32 atmospheres. From this work an empirical formulation was made for the tabulation of isotherms and isobars.

During the next few decades the only measurements were those of Trapeznikova and Shubnikov [13] in 1934 on an isotherm of 85°K, and the static measurements of Sagenkahn and Fink [14] at 1 and 2 atm in 1944.

Little else was done until 1955 when Armstrong and his colleagues at the National Bureau of Standards used a circulation method to make accurate determinations of the compositions and vapor pressures at 65, 70, and 77.5°K [15]. Two years later Cockett conducted extensive measurements at 1.3158 atmospheres

[16] with results reasonably close to those of Dodge and Dunbar.

Recent significant measurements are those of Din [17] who used the static method for nine intermediate mixtures at pressures to 10 atm. His results likewise show those of Dodge and Dunbar to be reasonable as do the experiments of Latimer [18] in 1957. In 1961 Yendall and Olzewski followed with a report on the saturation properties of nitrogen-oxygen mixtures [19].

The WADD Technical Report of 1961 [20] presents a compilation of the data of Armstrong et al, Dodge and Dunbar and Sagenkahn and Fink on T-x diagrams. The data of Sagenkahn and Fink at 1 and 2 atm and of Cockett at 1.3158 atm are presented on P-x diagrams. The graphics use a base of Hilsenrath's [21] pure component vapor pressure values. Tables of selected experimental values of all of the above are given.

Air Product and Chemicals, Inc. also published under government contract a technical report [22] with a P-T diagram of vapor and liquid curves based on the data of Dodge and Dunbar for the two-phase region and the vapor pressure data of Hoge for oxygen [23] and Michels et al, Friedman and White, Dodge and Davis, and Henning for nitrogen [24,25,26,27]. The critical envelope is based on the work of Kuenen et al [28,29] and can be considered precise to $\pm 2^{\circ}\text{K}$. The work of Kuenen et al also indicates the presence of retrograde condensation over small ranges near the critical points.

The most recent work is that of Haselden and Thorogood in 1963 at high oxygen concentrations [30] which showed a good correlation with the earlier works of Din and Latimer below 96 %mole oxygen. They demonstrated, however, that the relative volatility falls off at high oxygen concentrations. This is alleged to be

indicative of the occurrence of association, that is, the weak chemical interaction between the oxygen and nitrogen molecules.

For the work at hand, reliance has been placed primarily in the data of Dodge and Dunbar, because it is considered to be consistent and detailed over a wide range of values. Their data can be considered accurate to $\pm 0.1^\circ\text{K}$ at pressures near atmospheric and to about $\pm 1^\circ\text{K}$ at pressures above seven atmospheres [22]. Saturation values for the pure components have been taken for this work from Stewart for oxygen [31] and Strobridge for nitrogen [32], since the data of these investigators was used for all other pure component property values. Stewart's empirical vapor pressure equation was fitted to the data of Hoge [23] while that of Strobridge fits the data of Friedman and White [25] and Armstrong [33].

Individual temperature-composition diagrams have been drawn for 1, 5, 10 and 20 atm and are presented in Appendix A.

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The Virial Equation

The virial equation of state is simply a series expansion of the compressibility factor in terms of density.

$$Z = \frac{PV}{RT} = 1 + \frac{B(T,x)}{V} + \frac{C(T,x)}{V^2} + \frac{D(T,x)}{V^3} + \dots \quad (2)$$

Because of the molecular interactions, the virial coefficients are functions of both temperature and composition and can be written as [1]

$$B_m = B(T,x) = \sum_{i=A}^n \sum_{j=A}^n x_i x_j B_{ij} \quad \text{and} \quad (3)$$

$$C_m = C(T,x) = \sum_{i=A}^n \sum_{j=A}^n \sum_{k=A}^n x_i x_j x_k C_{ijk} \quad (4)$$

For a binary mixture these become

$$B_m = x_A^2 B_{AA} + 2x_A x_B B_{AB} + x_B^2 B_{BB} \quad \text{and} \quad (5)$$

$$C_m = x_A^3 C_{AAA} + 3x_A^2 x_B C_{AAB} + 3x_A x_B^2 C_{BBA} + x_B^3 C_{BBB} \quad (6)$$

where x_A is the mole fraction of component A.

Molecular theory tells us that for non-polar molecules (angle independent molecules possessing no permanent charge distribution) such as those being investigated, calculation of their virial coefficients depends on the choice of proper potential functions. The potential function represents the attractive and repulsive forces between molecules and many are found in the literature [2, 3]. Although these forces are generally exponential in char-

acter, they have generally been simplified to reciprocal power forms.

The most popular relationship is of the form

$$U(r) = K_1 r^{-n} - K_2 r^{-m} \quad (7)$$

where the first term represents the repulsive potential energy and the second that of the attractive contribution. Where \underline{n} and \underline{m} are chosen as 12 and 6 respectively there results the well known Lennard-Jones potential (compare with Eq. 1).

$$U(r) = 4\epsilon (\sigma/r)^{12} - (\sigma/r)^6 \quad (8)$$

It can be shown [4] that by using the Lennard-Jones potential the pure component virial coefficients can be expressed as

$$B(T) = f(T^*, b_0) \quad \text{or} \quad B^*(T) = B(T)/b_0 = f(T^*) \quad (9)$$

where b_0 is the "hard sphere" volume defined by $(2/3)\pi N \sigma^3$ and $T^* = T/(\epsilon/k)$. Similarly

$$C^*(T) = C(T)/b_0^3 = f(T^*/\epsilon/k) \quad (10)$$

Eqs. (9) & (10) have both been tabulated and plotted.

The interaction or cross virial coefficients are significantly more difficult to determine. For an ideal solution obeying Amagat's Rule [5]

$$\left. \begin{aligned} B_{AB} &= (B_{AA} + B_{BB})/2 \\ C_{AAB} &= (2C_{AAA} + C_{BBB})/3 - (B_{AA} - B_{BB})^2 \\ C_{ABB} &= (C_{AAA} + 2C_{BBB})/3 - (B_{AA} - B_{BB})^2 \end{aligned} \right\} \quad (11)$$

which is the Lewis-Randall rule for mixtures of simple gases and results in the following for a binary mixture:

$$\left. \begin{aligned} B_x &= x_A B_{AA} + x_B B_{BB} \quad \text{and} \\ C_m &= x_A C_{AAA} + x_B C_{BBB} - 3x_A x_B (B_{AA} - B_{BB})^2 \end{aligned} \right\} \quad (12)$$

It has been shown [6], however, that as $B_{AA}(T)/\sigma_{AA}^3$ is a universal function of kT/ϵ_{AA} , so too is $B_{AB}(T,x)/\sigma_{AB}^3$ a function of kT/ϵ_{AB} . The measurement of second virials in mixtures of dilute gases where the third virials are negligible can be used to verify the various combining rules derived on the basis of this relation. The most popular and simple of these are the Lorentz-Berthelot rules [7]

$$\epsilon_{AB} = (\epsilon_{AA} \epsilon_{BB})^{1/2} \quad \text{and} \quad \sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2 \quad (13)$$

which is based on London's theory of dispersion energy [8,9,10]. These rules give a better account of the second virial coefficient of simple gases than the Lewis-Randall rule, yet there is real doubt [4] whether any rule will yield accurate values of B_{AB} even under the best conditions of small, non-polar and spherically symmetric molecules. To make matters worse, very few experimental measurements of second virial coefficients have been made on mixtures of simple molecules. Newer and more accurate functions such as the Kihara potential are presently coming under more and more study [11,12,13,14].

When consideration is on mixtures other than dilute gases, no exact relation is available to correlate the interaction energies. Present practice [6] is to extend the principle by

considering an average interaction energy

$$\langle U_{AB}(r) \rangle / \epsilon(x) = f \left[r / \sigma(x) \right] \quad (14)$$

While the virial equation provides the best theoretical basis for estimating the PVT properties of mixtures, it cannot deal satisfactorily with any but low pressure gas mixtures. The inability to estimate third and higher virial coefficients generates an overall loss of accuracy.

The thermodynamic properties of enthalpy and entropy are derivable from the virial equation [4,15,16,17]. From the First and Second Laws for a single-component, closed system $dE = TdS - PdV$ and $H \equiv E + PV$ whence $dH = TdS + VdP$. If this last is divided by dP and T is held constant, the relation $(\partial H / \partial P)_T = V - T(\partial V / \partial T)_P$ results. If $Z = PV/RT$, then $(\partial H / \partial P)_T = (-RT^2/P)(\partial Z / \partial T)_P$ or after integration

$$(H_2 - H_1)_T = -RT^2 \int_{P_1}^{P_2} (\partial Z / \partial T)_P d(\ln P) \quad (15)$$

If $P_1 = 0$ and $T_r = T/T_c$, $P_r = P/P_c$, then

$$(H - H^0)/RT_c = -T_r^2 \int_0^{P_r} (\partial Z / \partial T_r)_{P_r} d(\ln P_r) \quad (16)$$

where $(H - H^0)$ is the enthalpy change from $P=0$ to $P=P$ at constant temperature. Then for mixtures [3], Eqs. (2) & (15) give

$$(H_m - H_m^0)/RT = 1/V \left[B_m - TdB_m/dT \right] + 1/V^2 \left[C_m - T/2(dC_m/dT) \right] + \dots \quad (17)$$

From the Maxwell relation $(\partial S / \partial P)_T = (\partial V / \partial T)_P$ and $Z = PV/RT$ we have $(\partial S / \partial P)_T = -R/P \left[Z + T(\partial Z / \partial T)_P \right]$. Since the entropy blows up as pressure goes to zero, it is convenient to use the artifice of integrating this relation as a real gas to a pressure near

zero where properties approximate those of a perfect gas. The equation is then integrated using perfect gas properties up to a convenient reference pressure, P_s , so that low pressure effects on the entropy mutually cancel [4]. Then

$$(S-S_s)/R = \int_0^P (1-Z) d(\ln P) + \ln(P_s/P) - T \int_0^P (\partial Z / \partial T)_P d(\ln P) \quad (18)$$

or in reduced terms

$$(S-S_s)/R = \int_0^{P_r} (1-Z) d(\ln P_r) + \ln(P_{rs}/P_r) - T_r \int_0^{P_r} (\partial Z / \partial T_r)_{P_r} d(\ln P_r) \quad (19)$$

where $(S-S_s)/R$ is the entropy change from

T, P_s to T, P or T_r, P_{rs} to T_r, P_r . Then, Eq. (2) & Eq. (18) give

$$(S_m - S_{ms})/R = -\ln P_s - T/V [dB_m/dT] - B_m^2/2V^2 + C_m/2V^2 - T/2V^2 [dC_m/dT] \quad (20)$$

Values can be determined for dB/dT by differentiating curves of $B^*(T)$ as a function of T^* , using the relation $dB^*/dT^* = (\epsilon/k/b_0) dB/dT$.

Finally to determine H_m and S_m the relations

$$H_m^O = \sum_i x_i H_i^O \quad \text{and} \quad S_{ms} = \sum_i x_i S_{is} - R \sum_i \ln x_i + R \ln P_s \quad (21)$$

can be used, where H_i^O is the enthalpy of component i at $P=0$ and S_{is} is the entropy of component i at reference pressure, P_s .

The virial equation is not the most convenient method of determining the thermodynamic properties of mixtures unless computer facilities are available. If a virial equation has been formulated for PVT properties, however, it would not require much additional effort to program the derivatives of the equation.

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Pseudocritical Properties

It was stated earlier that the molecular energies of interaction could be described by their dependencies on a universal

function as expressed by Eq. (14). The molecular theories of Prigogine et al [1] in which explicit relations for the parameters $\epsilon(x)$ and $\sigma(x)$ are developed in terms of their pure and mixture forms, ie, $\epsilon_{AA}, \epsilon_{AB}, \epsilon_{BB}, \sigma_{AA}, \sigma_{AB}, \sigma_{BB}$, through the Lennard-Jones or other m-n potential forms, are formally equivalent to the pseudocritical methods of Kay et al [2]. The relations $kT/\epsilon(x)$ and $V/\sigma^3(x)$ are equivalent to universal functions which may be replaced by $T/T_c(x)$ and $V/V_c(x)$, where $T_c(x)$ and $V_c(x)$ are pseudocritical properties of the mixture [3]. The pseudocritical concept is based on the existence of a mythical pure fluid at the temperature and pressure of the mixture which exhibits the same properties as the mixture. The critical properties of this fluid are the pseudocritical properties of the mixtures.

A sizable amount of literature has been written on the determination and use of the pseudocritical constants [2,4,5,6,7]. Kay's simple mole fraction averaging rules [2] are the most frequently used; in fact, the various rules for pseudocritical temperature all reduce under various simplifications to that of Kay. If $T_{cm} \equiv T_c(x)$, Kay's rules are given by

$$T_{cm} = \sum_i x_i T_{ci} \quad (22) \quad \text{and} \quad P_{cm} = \sum_i x_i P_{ci} \quad (23)$$

For T_{cm} , Kay's rule produces values within 2% of other rules for $0.5 < T_{CA}/T_{CB} < 2.0$ and $0.5 < P_{CA}/P_{CB} < 2$ [8]. For values of P_c differing by 20% or more, the modified Prausnitz and Gunn rule [9] should be used.

$$P_{cm} = Z_{cm} RT_{cm} / V_{cm} = R \sum_i x_i Z_{ci} \sum_i x_i T_{ci} / \sum_i x_i V_{ci} \quad (24)$$

Kay's rule has been verified to predict the true critical temperature of N_2-O_2 mixtures to within $10^\circ K$.

Using the pseudocritical rules for mixtures of nitrogen and oxygen, the author computed enthalpy deviations by the method suggested by Reid & Sherwood. A summary of this method follows:

1. Pseudocritical constants for the mixture were calculated from the following pure component values:

	Nitrogen	Oxygen
T_c	$126.26^\circ K$ [11,14]	$154.77^\circ K$ [12,13]
P_c	33.54 atm [11,14]	50.14 atm [12,13]
V_c	90.07 cm ³ /mole [15]	$.075$ cm ³ /mole [12]
Z_c	$.291$ [8]	$.292$ [8]

2. Base enthalpies, $H_{T_o}^o$, for nitrogen and oxygen were selected based on the enthalpies of the perfect gas at 1 atm at the normal boiling point and triple point respectively [11,12].
3. The ideal state enthalpies at the various isotherms of interest, H_T^o , are then calculated from

$$H_T^o = H_{T_o}^o + \int_{T_o}^T C_p^o dT \quad (25)$$

where $C_{pN_2}^o = 29.121$ j/mole^oK and $C_{pO_2}^o = 29.359$ j/mole^oK [16].

4. At a particular temperature the perfect gas mixture enthalpies, H_m^o , may be calculated from

$$H_m^o = \sum_i x_i H_{Ti}^o \quad (26)$$

5. The mixture enthalpy at the system pressure is then

$$H_m = (H_m - H_m^O) + H_m^O \quad (27)$$

where the isothermal enthalpy deviation $H_m - H_m^O$ can be determined from suitable tables [17].

Reid and Sherwood predict errors of 10% in the vapor phase and 20% in the liquid for this method [8]. This author carried out calculations at 84°K and 1 atm and at 112°K and 10 atm. In the vapor phase for the case of 84°K and 1 atm, although the calculated values differed from those obtained using a mole fraction average of the pure component enthalpies by as much as 35 j/mole, the results were linear and had the same slope (Fig. 4a). In the liquid region at this temperature the results showed a small negative deviation from linearity (experimental evidence indicates a positive excess heat) with the absolute difference increasing with increasing %mole O₂ (Fig. 4b). At the higher pressure the calculated vapor isotherm was no longer linear, but exhibited a sizeable negative excess heat. Likewise the liquid isotherm at this pressure displays a somewhat larger contrary behavior than before. All isotherms are extrapolated into the wet vapor region. These calculations seemed to be undesirable for their deviations from known behavior, ie, negative excess heat. The tables offer, however, a relatively simple computational technique and are applicable to the liquid phase as well as the vapor. Perhaps better values of the pseudocritical properties would produce more logical results, but for the present, simple mole fraction averaging seems to provide more satisfactory answers.

While tables such as those of Lyderson et al do not exist for entropy deviations from the perfect gas base, a relationship can

Figure 4a.

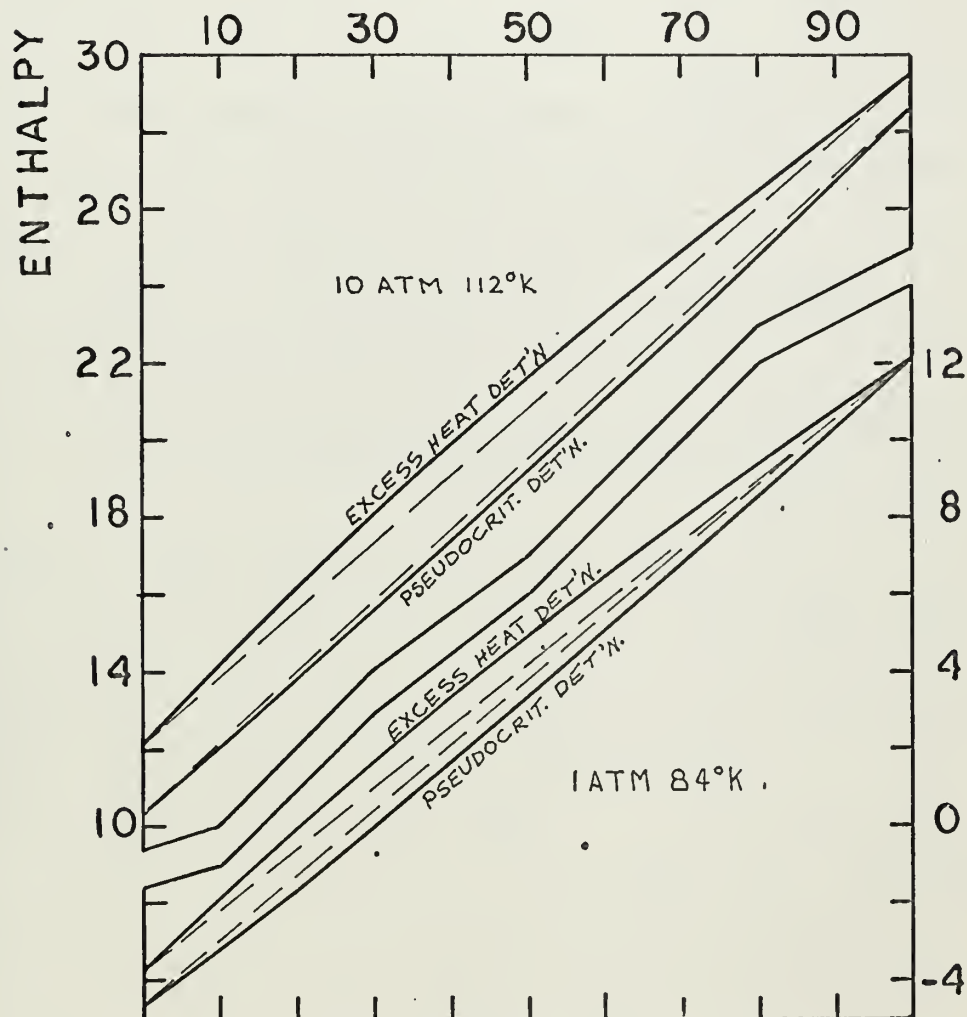
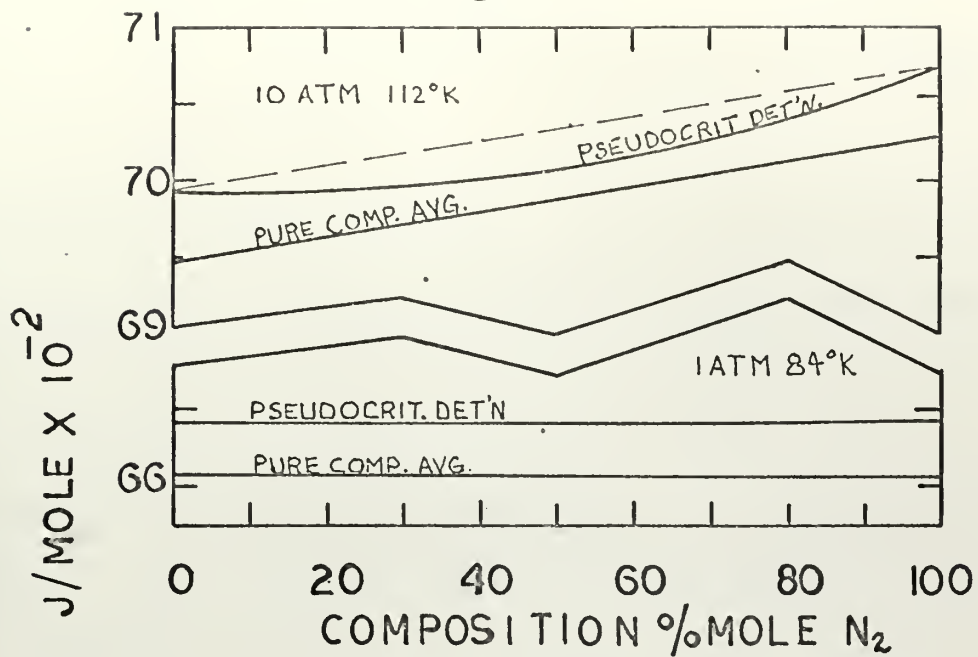


Figure 4b.

Figure 4a & 4b. Liquid and vapor lines determined by various methods. Dashed lines join pure component values:

be written between properties of other values which are tabulated.

Eq. (18) can be written [8]

$$(S - S_S)/R = (H - H^0)/RT - \ln(f/P_S) \quad (28)$$

when $P=P_S$ and values of both $(H - H^0)$ and (f/P_S) have been tabulated.

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Empirical Equations of State

Perhaps the most underdeveloped of the techniques for the determination of the properties of mixtures is that of a workable equation of state, particularly in the two-phase region.

The Benedict-Webb-Rubin equation [1] with eight constants has been fruitfully tested, but unfortunately is applicable only to light hydrocarbon mixtures.

Some effort has been made to determine coefficients for the two constant Redlich-Kwong equation [2] as follows:

$$\left[P + a/[T^{0.5}V(V+B)] \right] (V - b) = RT \quad (29)$$

where for a mixture $a_m^* = \sum_i x_i a_i^*$ and $b_m^* = \sum_i x_i b_i^*$

and also $a_i^{*2} = 0.4278/T_{ri}^{2.5} P_{ci}$ and $b_i^* = 0.0867/T_{ri} P_{ci}$

It is reported that some success has been obtained in using reduced temperatures and pressures derived from Kay's rules in the generalized Beattie-Bridgman equation [3].

$$P_r = (T_r/V_{ri}^2)(1 - 0.05/T_r^2 V_{ri}) \left[V_{ri} + 0.1867 \left[(1 - 0.03833)/V_{ri} \right] \right] \\ - (0.4758/V_{ri}^2) \left[(1 - 0.1127)/V_{ri} \right] \quad (30)$$

Recent efforts [4,5] have been fairly successful in treating gas mixtures of CO_2 and N_2 with mixture rules for the Martin-Hou equation of state.

$$P = \sum_{i=1}^5 f_i (V - b)^{-i} \quad \text{where } f_i = A_i + B_i T + C_i \exp(k' T/T_c) \quad (31)$$

None of the equations of state have been extensively tested with mixtures, with the possible exception of the BWR equation for light hydrocarbons, and all require machine handling. In the derivation of thermodynamic properties using Eqs. (15) & (18) the results will be only as good as the equation used, and sometimes worse, because of the errors involved in the determination of the derivatives of the equation.

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Partial Properties

It was mentioned earlier that use might be made in some cases of partial properties in determining mixture properties. Partial molar properties define the properties of components in a mixture as opposed to those of the pure components and represent a part of the total property of the particular mixture. In particular, a property is defined as

$$\bar{R}_i = (\partial R / \partial n_i)_{n \neq i, P, T} \quad \text{or} \quad R = \sum_i n_i \bar{R}_i \quad (32)$$

where R is any extensive property and n_i is the number of moles of component i in the mixture. These relations are governed by

the Gibbs-Duhem equation

$$\sum_i n_i d\bar{R}_i = 0 \quad (33)$$

If $\bar{R} = R/n = \sum_i x_i \bar{R}_i$, then it can be shown [1] that

$$\bar{R}_A = \bar{R} - x_B (\partial \bar{R} / \partial x_B) \quad \text{and} \quad \bar{R}_B = \bar{R} - x_A (\partial \bar{R} / \partial x_A) \quad (34)$$

The Lewis relation [2] for fugacity as it is related to the chemical potential can be expressed for a mixture as

$$\mu_i \equiv (\partial G / \partial x_i)_{x_{\neq i}, P, T} = RT \ln \bar{f}_i + \theta_i(T) \quad (35)$$

where $\theta_i(T)$ is some function of temperature only. As the pressure approaches zero, \bar{f} approaches P_i as opposed to the chemical potential which blows up as can be seen from $(\partial \mu_i / \partial P)_T = \bar{V}_i$. At constant temperature and composition Eq. (35) can be written [3,4]

$$RT \ln(\bar{f}_i / f_i^V x_i^V) = \int_0^P (\bar{V}_i - V_i) dP \equiv RT \ln \gamma_i \quad (36)$$

where γ_i is defined as the activity coefficient. For ideal solutions this reduces to the Lewis & Randall rule [2]

$$\bar{f}_i = x_i^L f_i^L \quad \text{such that} \quad \gamma_i = 1. \quad (37)$$

While in an ideal solution it is only necessary that the intermolecular forces be the same for all components, in a perfect gas the molecular forces must be zero. In this case the pure component fugacities are equal to the pressure and Raoult's law results:

$$\bar{f}_i = \bar{P}_i = x_i^V P \quad (38)$$

It should be mentioned that the Lewis-Randall rule generally provides a good approximation for most real non-polar gas mixtures at any pressure as long as the component in question is similar to the other component or present in excess of the other component [5].

If the fugacity of the pure components in the mixture can be determined, the enthalpy deviation representing the non-ideality of the mixture can be determined from the relation

$$- \left[\partial \left[\ln(\bar{f}_i / x_i P) \right] / \partial T \right]_{P,x} = (\bar{H}_i - H_i^O) / RT^2 \quad (39)$$

The mixture enthalpy then, follows from the partial property and perfect gas base state relation

$$H_m = \sum_i x_i (\bar{H}_i - H_i^O) + \sum_i x_i H_i^O \quad (40)$$

where the pure component perfect gas values are determined as before.

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Excess Functions

Before discussing deviations from ideality, it would do well to define somewhat more fully the ideal mixture. One definition [1] states that it is a mixture whose components have chemical potentials given by

$$\mu_i(P, T, x) = \mu_i(P, T) + RT \ln x_i \quad (41)$$

where $\mu_i(P, T)$ is the pure component potential at the pressure and temperature of the mixture. It follows that for an ideal mixture

$$\left. \begin{aligned} G &= \sum_i x_i \mu_i + RT \sum_i x_i \ln x_i \\ H &= \sum_i x_i H_i \\ S &= \sum_i x_i S_i - R \sum_i x_i \ln x_i \\ V &= \sum_i x_i V_i \end{aligned} \right\} \quad (42)$$

The log sums are referred to as the ideal free energy of mixing, G^m , and the ideal entropy of mixing (Gibbs paradox), S^m . The ideal free energy of mixing is always negative and that of entropy always positive. The ideal enthalpy and molar volume of mixing are equal to zero.

Excess properties may be defined in these terms as the differences between the values of the properties in the real mixture and the values of the properties given by Eqs. (42) for an ideal mixture of the same composition.

It has been seen that the chemical potential may be related to the activity coefficient, so that for a real mixture at low pressures

$$\mu_i(P, T, x) - \mu_i(P, T) = RT \ln x_i \gamma_i \quad (43)$$

The partial molar properties may then be given by

$$\left. \begin{aligned} \bar{H}_i &= H_i - RT^2 (\partial \ln \gamma_i / \partial T)_P \\ \bar{S}_i &= S_i - R \ln x_i \gamma_i - RT (\partial \ln x_i / \partial T)_P \\ \bar{V}_i &= V_i + RT (\partial \ln \gamma_i / \partial P)_T \end{aligned} \right\} \quad (44)$$

The excess thermodynamic properties may then be obtained by subtracting the ideal quantities from the partial molar quantities.

$$\left. \begin{aligned} G^E &= RT \sum_i x_i \ln \gamma_i \\ H^E &= RT^2 \sum_i x_i (\partial \ln \gamma_i / \partial T)_P \\ S^E &= -R \sum_i x_i \ln(x_i \gamma_i) - RT \sum_i x_i (\partial \ln \gamma_i / \partial T)_P \\ V^E &= RT \sum_i x_i (\partial \ln \gamma_i / \partial P)_T \end{aligned} \right\} \quad (45)$$

The excess functions are related by

$$G^E = H^E - TS^E = H^E + T(\partial G^E / \partial T)_P \quad (46)$$

Considerable effort has been made in the past decade in the measurement of excess functions. In particular, regarding N_2 - O_2 mixtures, Knobler et al [2,3,4] measured H^E and V^E at 77°K; Wilhelm & Schneider [5], G^E at 77.5°K; Pool et al [6], G^E at 83.8°K;

and Duncan & Staveley [7], G^E at 63.14°K. In addition, values of G^E have been calculated by some of these authors from the vapor pressure measurements of Dodge & Dunbar [8], Armstrong et al [9], and Din [10]. These results are plotted in Fig. 32 for equimolar liquid mixtures.

It can be shown [1] that the variation of vapor pressure at constant temperature can be related to the excess Gibbs free energy. Vapor pressure and composition can be measured in an equilibrium still, a large number of which have been devised [11-24]. The principal problem in all stills is the difficulty in eliminating vapor condensation before it reaches the vapor sampling point and of preventing liquid droplets from being carried over to the same point. These problems can be eliminated by methods which utilize only the total static vapor pressure as a function of liquid composition. Then the vapor composition may be found analytically using the Gibbs-Duhem equation. Several methods have been used to measure the total vapor pressure [25-29].

If isothermal vapor pressure measurements are known, values of G^E may be derived from knowledge of P , x^l , x^v and the second virial coefficient. If the easier experimental procedure has been followed, which measures x^l and not x^v , there are several graphic, algebraic, and machine methods which may be used to solve for G^E [27,30-35]. These solutions are more complicated than those used when both compositions have been measured. Other methods have been devised for the calculation of the liquid composition, if only the vapor composition has been measured [36-38]. Finally, if all four properties are known, then the thermodynamic consistency

of the results may be tested with the Duhem-Margules equation [39].

The most widely used test for consistency is that developed by Coulson & Herington [40] and by Redlich & Kister [41]. If the volatility ratio is defined by $\alpha \equiv x_B^v/x_A^v / x_B^l/x_A^l$ where B is the more volatile component, then the difference in excess chemical potentials of two components can be given as

$$\mu_B^E - \mu_A^E = RT \ln(\gamma_B/\gamma_A)^l = (\partial G^E/\partial x_B^l)_T = RT \ln(\alpha P_A/P_B) + (P - P_A)$$

$$(V_A^l - B_{AA}) - (P - P_B)(V_B^l - B_{BB}) + 2P(\delta_B)_{AB}(x_A^{v2} - x_B^{v2}) \quad (47)$$

By integrating this expression over x_B^l , where G^E is zero at $x=0$ and $x=1$, we obtain

$$\int_0^1 \ln(\alpha P_A/P_B) dx_B^l = 1/RT \int_0^1 \left[(P - P_B)(V_B^l - B_{BB}) - (P - P_A)(V_A^l - B_{AA}) - 2P(\delta_B)_{AB}(x_A^{v2} - x_B^{v2}) \right] dx_B^l \quad (48)$$

If the results are consistent, the volatility ratio will equal the pure component pressure ratio, ie, $\alpha = P_B/P_A$, at the composition where G^E is a maximum or a minimum value in a non-ideal mixture in equilibrium with a perfect gas. Therefore, by plotting $\alpha P_A/P_B$ as a function of x_B^l the areas above and below the axis will cancel if the results are consistent.

Unfortunately, it has been demonstrated [28] that this test fails for liquid mixtures in the vicinity of their normal boiling points, because it assumes that the vapor behaves as a perfect gas. Rowlinson [1] modified the method by noting that $(\delta_B)_{AB}$ made no significant contribution and that P could be replaced by Raoult's law pressure, $x_A^l P_A + x_B^l P_B$, so that

$$\int_0^1 \ln(\alpha P_A/P_B) dx_B^1 = [(P_A - P_B)(V_A^1 - V_B^1 - B_{AA} - B_{BB})] / 2RT \quad (49)$$

an explicit relation which is convenient to use.

The most widely noted method of determining G^E from measured isothermal values of total pressure and liquid composition is that of Barker [41]. This author has made calculations of G^E for N_2 - O_2 mixtures at intervals of $10^\circ K$ from $80^\circ K$ to $120^\circ K$ using this method. The procedure is outlined for interest in Appendix B.

Rowlinson [1] has indicated the difficulty in defining the excess free energy at vapor pressures greater than 2 to 3 atm, because of compressibility effects. This can be seen in Fig. 32 where the values of G^E calculated by the author have been plotted with those calculated by other investigators at lower temperatures. It should be noted, however, that the slope of the values between 100 and $120^\circ K$ (dashed line) is identical to that at lower temperatures (solid line), and one wonders if perhaps a method for calculating G^E including the third virial coefficient might not displace these values into line.

At any rate, studies in the vicinity of the two-phase region at pressures higher than atmospheric are virtually non-existent [1,43,44]. Even the molecular theorists have contented themselves with predictions of excess functions in the liquid phase at negligible pressures or when venturing into the field have confined themselves to predictions of relations for the critical constants. In the gas phase preoccupation has been with determining an equation of state [45] and almost no experimental work has been done to determine excess properties of gases. Only very recently have badly needed measurements on dense gases been attempted [46,47].

It had been generally felt [44] that the molecular theory would stand up well in the estimation of excess functions of mixtures of condensed gases, that is, liquid mixtures of simple molecules at temperatures near the boiling points of the mixtures. In the past decade, however, experimental work by Beenakker et al [2,3,4] and Staveley et al [6,7] have shown serious inconsistencies and plaguing weaknesses in the molecular methods. They have found that values of excess energy calculated by the molecular theory of Prigogine et al [43] are strongly dependent on both the set of potential parameters chosen and on the pure component selected as a "reference" substance.

The most probable cause of failure of the theory is considered to be the Lennard-Jones potential [6,7,48,49,50] particularly at the close molecular distances involved in liquids. Still another cause may lie in the inaccuracy of the interaction parameter combining rules. At any rate, the spectacular differences in the value of excess functions calculated from molecular theory from those measured experimentally is enough to preclude at this time consideration of values formulated by this means.

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Calorimetry

The measurement of the excess heat is of such importance as to deserve a separate section reviewing devices and methods presently available for its determination. The two principal instruments are the adiabatic and isothermal calorimeters. The adiabatic calorimeter reflects positive excess heat, if the temperature drops on mixing two pure components in an adiabatic container. If on mixing or afterwards heat is added to cancel out the temperature drop, the amount of excess heat can be measured. Heat added during mixing reduces corrections necessary for heat transfer to the environment. A similar determination may be made for negative excess heat with its indicative temperature rise.

The adiabatic calorimeter has been bothered by a variety of problems including imperfect heat isolation, incomplete mixing, inaccurate measurement devices, and spaces in which vapor can form. The last problem is complicated by the need to allow for volume changes on mixing.

Isothermal calorimeters have the advantage of not requiring corrections for heat losses or gains and are able to measure a greater temperature range accurately.

Many such devices are mentioned in the literature and some of the more important are listed here. Some early calorimetry at temperatures of about 100°K was done by Rowlinson & Malcolm [1]. A versatile instrument which can be used either isothermally or adiabatically has been developed by Nicholson [2]. A glass, highly accurate, apparatus is described by Larkin & McGlashan [3], which has eliminated vapor spaces, provided complete mixing and

allowed for expansion and contraction through a compensating piston. Likewise, Mrazek & Van Ness [4] in their equipment control the volume with close clearance pistons. Another novel control on volume change is the metal aneroid diaphragms of the device of Brown & Fock [5]. Work has been done with Bunsen isothermal calorimeters by some investigators [6,7]. Two recent calorimeters were specifically designed for measurements of condensed gas mixtures [8,9].

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Latent Heat

The latent heats of vaporization for mixtures are covered by a multitude of definitions [1,2]. The most obvious are the heats required for vaporization or condensation at constant pressure, constant temperature or constant composition.

One method of calculating the latent heat is by employing variations of the Clausius-Clapeyron relation [1,3-8]. One of

these variations expresses the differential heat of vaporization

$$\Delta V_{vl} dP - (\Delta H_{vl}/T) dT - (x^v - x^l) (\partial^2 G^l / \partial x^{l2})_{P,T} dx^l = 0 \quad (50)$$

for a small amount of vapor phase out of or into a large amount of liquid. Similarly, the differential heat of condensation is

$$\Delta V_{lv} dP - (\Delta H_{lv}/T) dT - (x^l - x^v) (\partial^2 G^v / \partial x^{l2})_{P,T} dx^v = 0 \quad (51)$$

for a small amount of liquid phase out of or into a large amount of vapor. The volume change is given by

$$\Delta V_{vl} = V^v - V^l - (x^v - x^l) (\partial V^l / \partial x^l)_{P,T} \quad (52)$$

and the heats are

$$\Delta H_{vl} = H^v - H^l - (x^v - x^l) (\partial H^l / \partial x^l)_{P,T} \quad (53)$$

and represent the heat required at constant temperature and pressure to obtain one mole of vapor phase from a large quantity of liquid or to condense one mole of vapor into a large amount of liquid. Similar expressions apply for ΔV_{lv} and ΔH_{lv} . Even with this seemingly straightforward approach there is no simple method of solution except with assumptions which ignore the effects of non ideality (see Graphical Methods).

Corresponding states theory yields an imposing array of estimation techniques for pure component latent heats [7]. Calculations were made by one of these methods [9], alleged to be among the most accurate and simple to apply, by adapting it to mixtures by use of the pseudocritical constants. This empirically derived relation can be expressed

$$(\Delta H_{vl})_b = [T_b(5 \log P_{cm} - 2.17)] / (0.93 - T_{br}) \quad (54)$$

where T_b is the normal boiling point and ΔH_{vl} is the isothermal differential heat of vaporization. The results, calculated at one atm, were less than satisfactory as can be seen in Fig. 31. In fact, because of the large latent heats as compared to the excess heats involved, it is a more accurate estimate simply to use the mole fraction average of the pure component latent heats, particularly at low pressures.

One experimental determination of the latent heats of N_2 - O_2 mixtures exist [10], a notable number when so few for any binary mixture can be found. Dana's measurements at atmospheric pressure are plotted in Fig. 31. They represent the integral heat of vaporization at constant pressure, that is, the heat required to change one mole of liquid to the vapor state under conditions of constant pressure and composition.

No matter how the heat of vaporization is determined, however, it is only as useful as the isotherm or phase boundary from which it will be based.

References for Latent Heat

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Graphical Methods

The earliest graphical techniques for determining the thermodynamic properties of N_2-O_2 mixtures were devised at the Kamerlingh Onnes Laboratory at the University of Leiden [1,2]. Keesom & Tuyn developed a general construction for H,S,x surfaces of the mixture in the two-phase region at atmospheric pressure. The property of the mixture that is the key to the geometric method is the transverse fold in the H,S,x-surface representing the wet vapor region. A tangent plane across the fold contacts the points of equilibrium or coexistent phases. These points were called connodes; the isotherm joining them, the nodal line; and the locus of these points, the connodal curves (vapor and liquid curves).

Basically, their procedure was to locate known points, such as the boiling point of oxygen on an H-S diagram, and with the aid of pure component heats of vaporization at 1 atm, the definition of enthalpy and entropy in terms of specific heat, ideal mixture rules, and Dodge and Dunbar equilibrium data [3], plot the vapor line which is then easily projected into the S-x plane.

Using the previously mentioned principle of tangent planes, the liquid line was determined in the H-S and S-x planes by

graphically constructing the line representing the plane tangent to the connodal points, assisted by Dana's heats of vaporization at constant composition [4]. The projection in the H-x plane was then easily established.

The procedure then recommends extrapolation in the H-S plane of the lines of constant composition to higher pressure using Second Law relationships and the virial equation of state, ie,

$$\left. \begin{aligned} dH &= V - T(\partial V / \partial T)_{P,x} dP \quad \text{and} \\ dS &= -(\partial V / \partial T)_{P,x} dP \end{aligned} \right\} (55)$$

which become with the application of the equation of state

$$\left. \begin{aligned} H &= (P_2 - P_1)(B - T dB/dT) \quad \text{and} \\ S &= R \ln P_1/P_2 - (P_2 - P_1) dB/dT \end{aligned} \right\} (56)$$

The ideal mixing rules locate the isocomposition lines between those of the pure components, and the equilibrium data fixes the end points at the vapor line. The form of the liquid line is then taken to be the same as that for one atm.

Lerberghe [5] proposed a variation on this method of his colleagues which requires only the use of the T-x equilibrium diagrams. From thermodynamics and analytical geometry, expressions were developed for the enthalpy and entropy difference between the connodal points.

$$\left. \begin{aligned} H^v - H^l &= (N + MT)(x^v - x^l) \quad \text{and} \\ S^v - S^l &= (L + M)(x^v - x^l) \end{aligned} \right\} (57)$$

$$\left. \begin{aligned}
 \text{where } L &= S_A^V - S_B^V + R \ln \left[(1 - x^V) / x^V \right] \\
 M &= -RT \left[1/(1-x^V) + 1/(x^V) \right] dx^V / dT \\
 N &= H_A^V - H_B^V
 \end{aligned} \right\} (58)$$

where the A and B are the pure component properties at the pressure and temperature of the mixture, extrapolated as necessary into the wet vapor region.

Thus by fixing the vapor line as was done by Keesom and Tuyn, Lerberghe's method locates the liquid line with the help of the equilibrium data. Note that the requirement exists to perform the difficult graphical tangent determination for dx^V/dT or to derive an equation for the vapor line on the T-x diagram by curve fitting and then taking its derivative analytically. Lerberghe's graphical measurements are reflected in Fig. 31 for the liquid line at one atm.

Several years later Bosnjakovic [6] nicely summarized various graphical procedures. His method suggests that in most cases the excess functions in the vapor phase can be neglected, at least in moderate pressures, and the isotherms in the H-x and S-x diagrams may be drawn according to the ideal mixture rules. Then, if the temperature-vapor composition relationship is known from equilibrium data, the vapor line is also determined in both planes.

In the liquid region, if the excess properties are known, then the isotherms may be drawn and the liquid line again determined as above for the vapor line. If the excess heat is not known, some estimation of the latent heat of vaporization must

be made. The Clausius-Clapeyron relation (Eq. 51) makes a good starting point. From the definition of Gibbs free energy the second derivative is given by

$$(\partial^2 G / \partial x^2)_{P,T} = (\partial^2 H / \partial x^2)_{P,T} - T (\partial^2 S / \partial x^2)_{P,T} \quad (59)$$

Then for an ideal vapor mixture

$$(\partial^2 G^V / \partial x^{V2})_{P,T} = RT/x^V(1-x^V) \quad (60)$$

Measurement of the slope of the T-x diagram graphically or analytically yields $(\partial x^V / \partial T)_P$. Enough information is then available to solve Eq. (51) for ΔH_{lv} at constant pressure and temperature. The vapor isotherm is then extended to intersect x^l and ΔH_{lv} is plotted from that point (Fig. 5). Repeating this process with isotherms of the wet vapor region yields the liquid line (Fig. 31). Obviously the method is sensitive to the behavior of the two differential terms of Eq. (51).

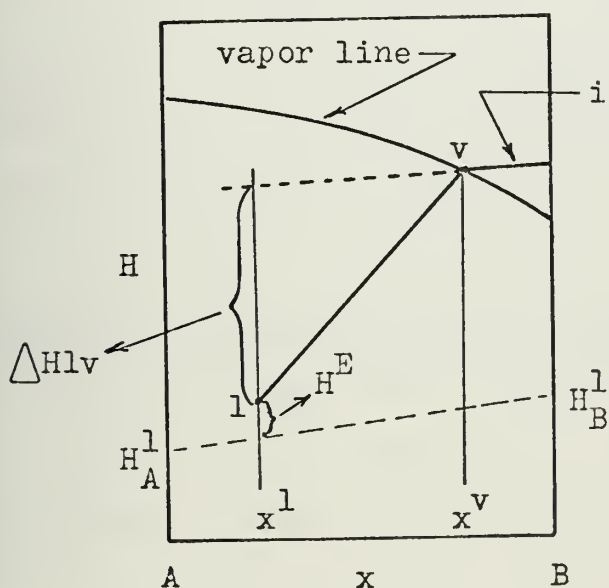


Figure 5

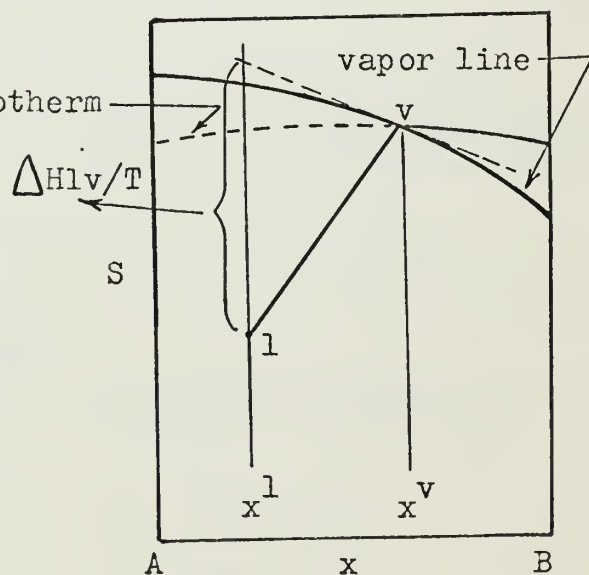


Figure 6

In the case of the S-x diagram, after the isotherms have been drawn according to the ideal mixing rules and the vapor line determined from equilibrium data, the liquid line may be determined from the relation

$$\Delta H_{lv}/T = S^l - S^v - (x^l - x^v)(\partial S^v / \partial x^v)_{P,T} \quad (61)$$

The value of $\Delta H_{lv}/T$ can be obtained from the H-x diagram and plotted from the intersection of the tangent to the vapor line at x^v with the equilibrium liquid composition, x^l (Fig. 6).

A secondary method of constructing the S-x diagram when the H-x diagram is available utilizes an integration procedure, which, needless to say, is less prone to graphical error than the differentiation technique. This method uses the relation that, for a reversible vaporization process at constant pressure and constant liquid composition,

$$(S^v - S^l)_{x^l} = \int_{T^l}^{T^v} 1/T (dH)_{x^l} \quad (62)$$

The right hand side of the equation may be easily integrated graphically using any of the several numerical integration rules and the difference measured from the known value of S^v .

References for the Graphical Methods

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The Thermodynamic Properties

The thermodynamic properties of binary mixtures of nitrogen and oxygen considered to be of the most value for use in engineering calculations are those of enthalpy and entropy. A useful format for the presentation of these properties is the graphical display, in particular the enthalpy-composition and entropy-composition diagrams at constant pressure. Accordingly Figs. 7-30 have been prepared for mixtures at pressures of 1, 5, 10, and 20 atm. Enthalpy and entropy have been represented as functions of composition in the liquid line region, the vapor line region, and the wet vapor region.

Values for the pure component oxygen were taken from Stewart's machine tabulation [1] based on a complex empirical expansion. Those for nitrogen came from the work of Strobbridge [2] whose machine tabulation is likewise based on an empirical equation of state.

The molecular weight of nitrogen was taken as 28.016 grams/mole [2] and one calorie as 4.184 abs. joules, by which conversion factors the tabulated values of Strobbridge were converted to abs. joules/mole.

For the sake of graphical convenience the properties of nitrogen and oxygen were equalized at 91°K at 1 atm, creating an oxygen enthalpy scale factor of 4245.3 j/mole and a nitrogen entropy scale factor of 81.12 j/mole. The values of entropy are

relative only, since the nitrogen scale is not based on zero entropy at absolute zero as is that of oxygen. Property values of the pure components within the two phase region have been linearly extrapolated.

Values of the entropy of mixing (Gibbs paradox) are derived from the relation

$$S^m = R \sum_i x_i \ln x_i \quad (63)$$

where R is the universal gas constant equal to 8.20574×10^2 L-atm/mole-°K [1].

Isotherms in the superheated vapor region were derived as mole fraction averages of the values for the pure components, ie, from the ideal mixture rules. The excess heat and entropy functions for the liquid isotherms were derived by the author from the data of several investigators (see Discussion of Results). The vapor and liquid lines were plotted using the isotherms and the temperature-composition data of Dodge and Dunbar [3].

References for Thermodynamic Properties

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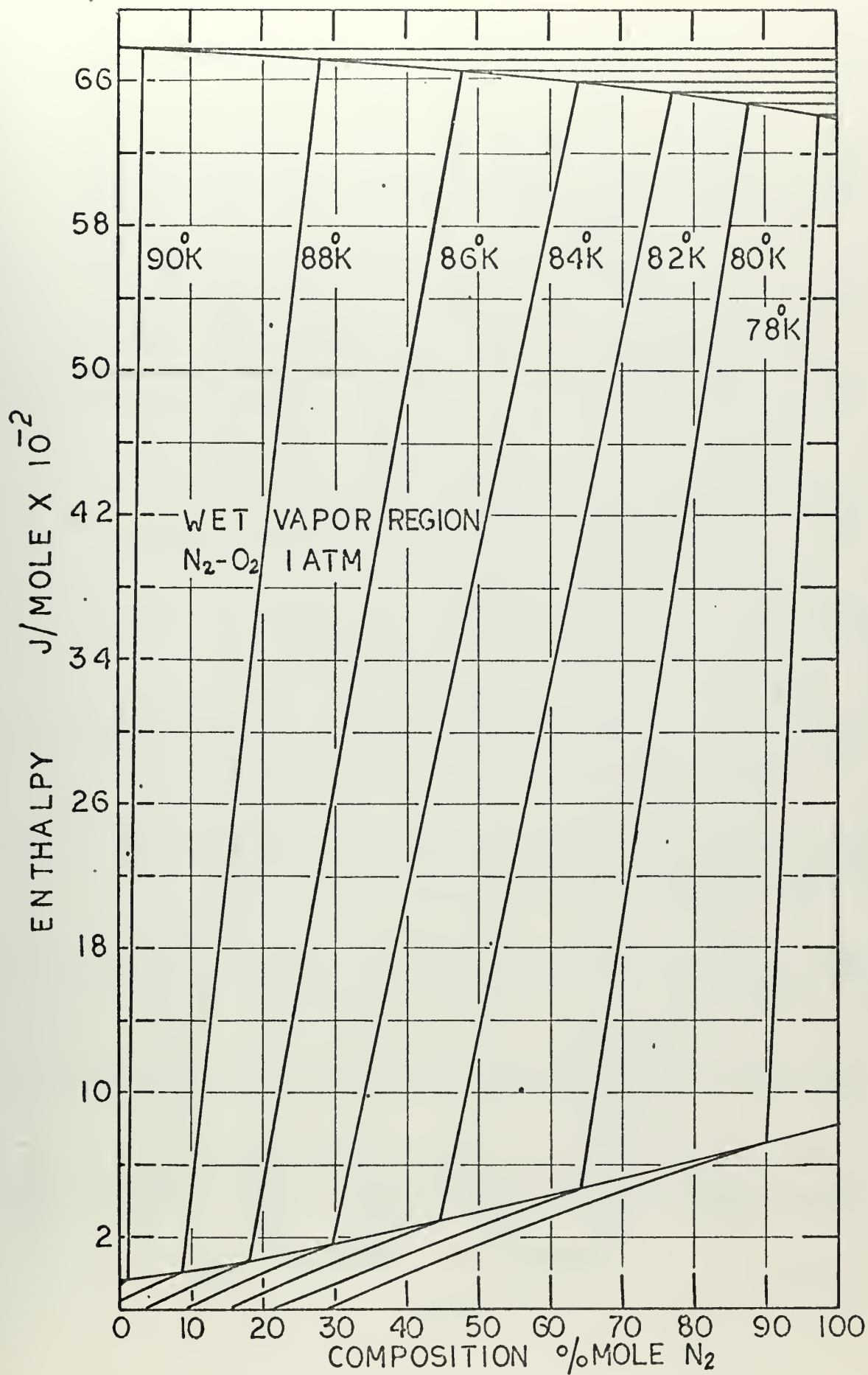


Figure 7.

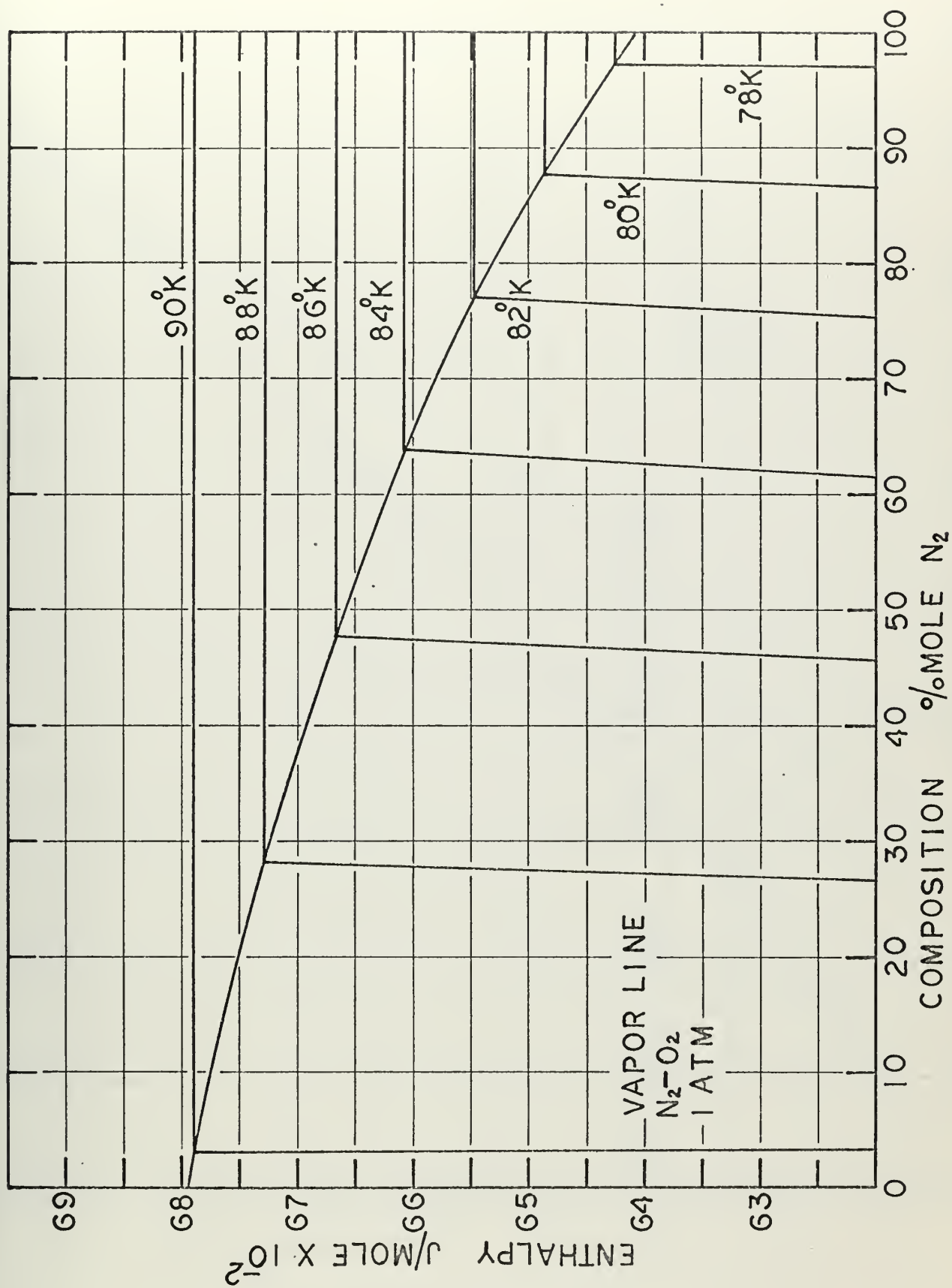


Figure 8

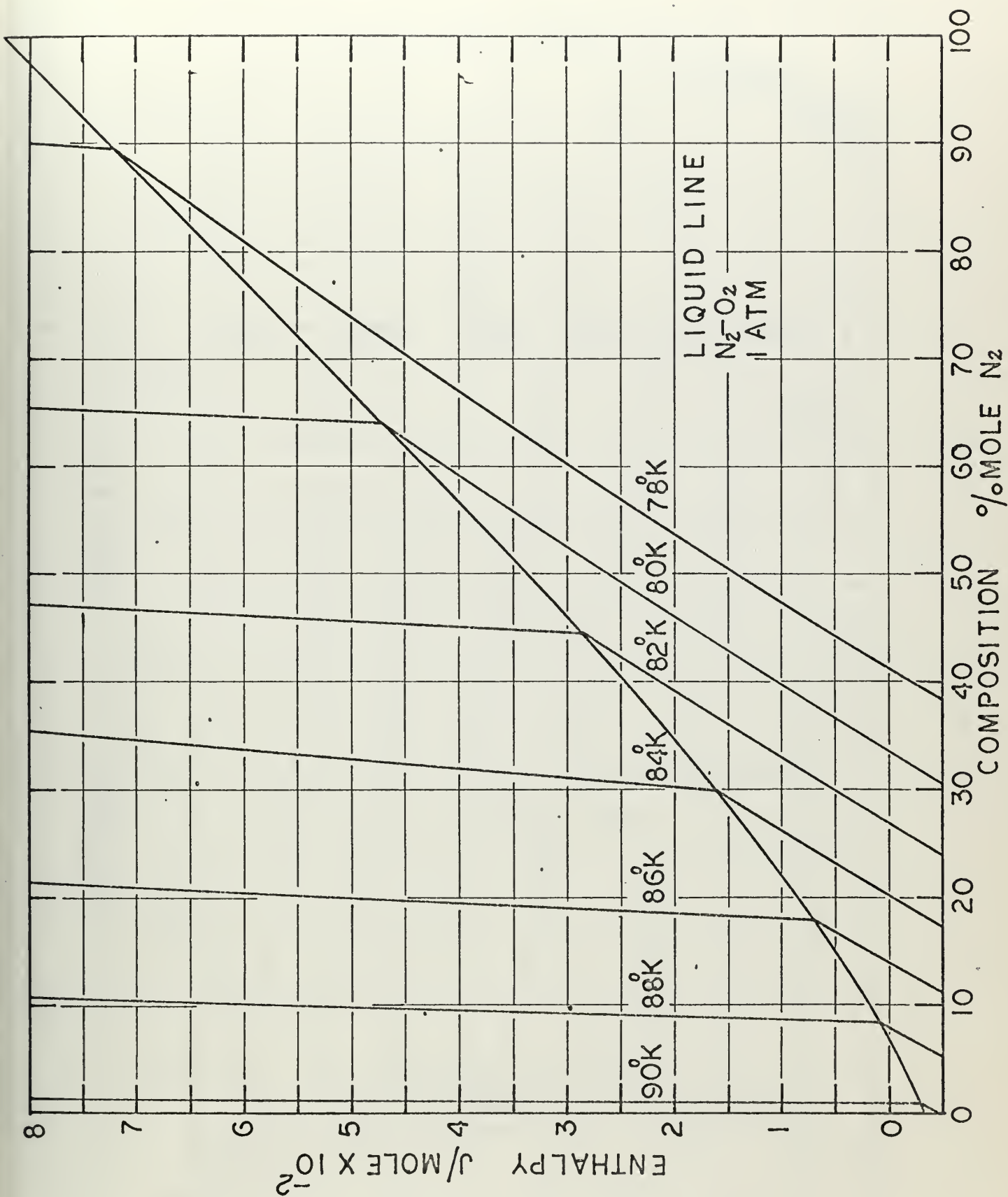


Figure 9

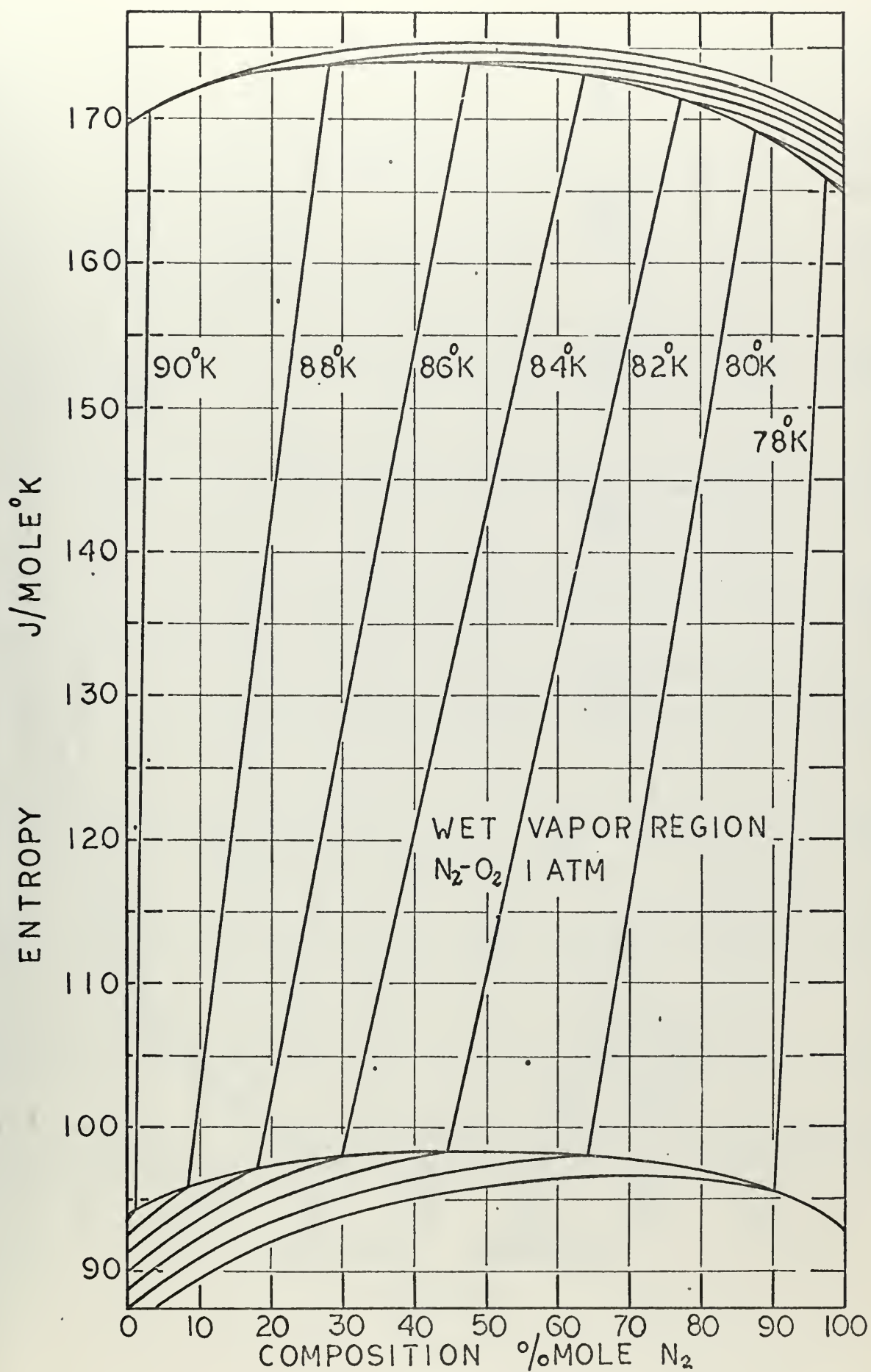


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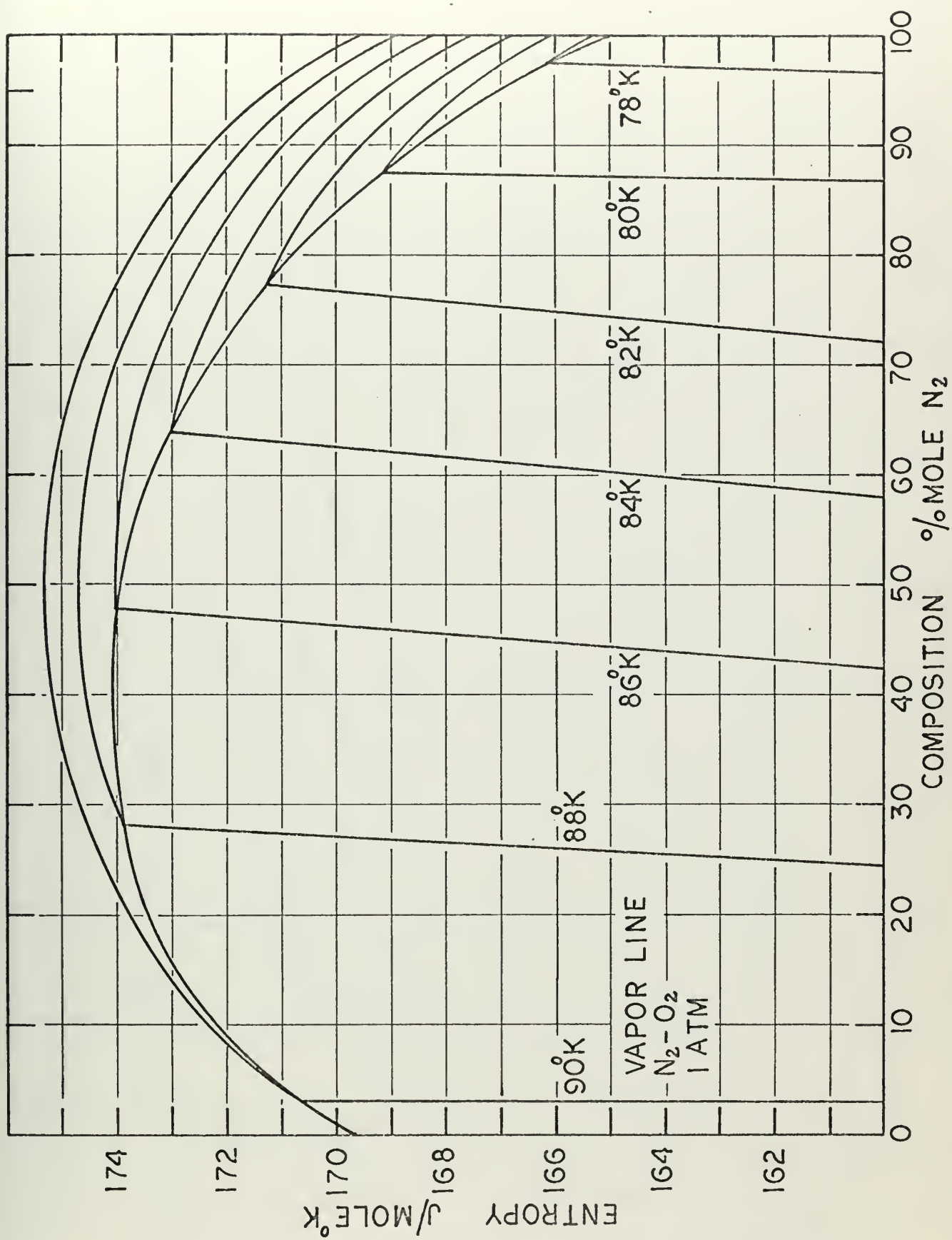


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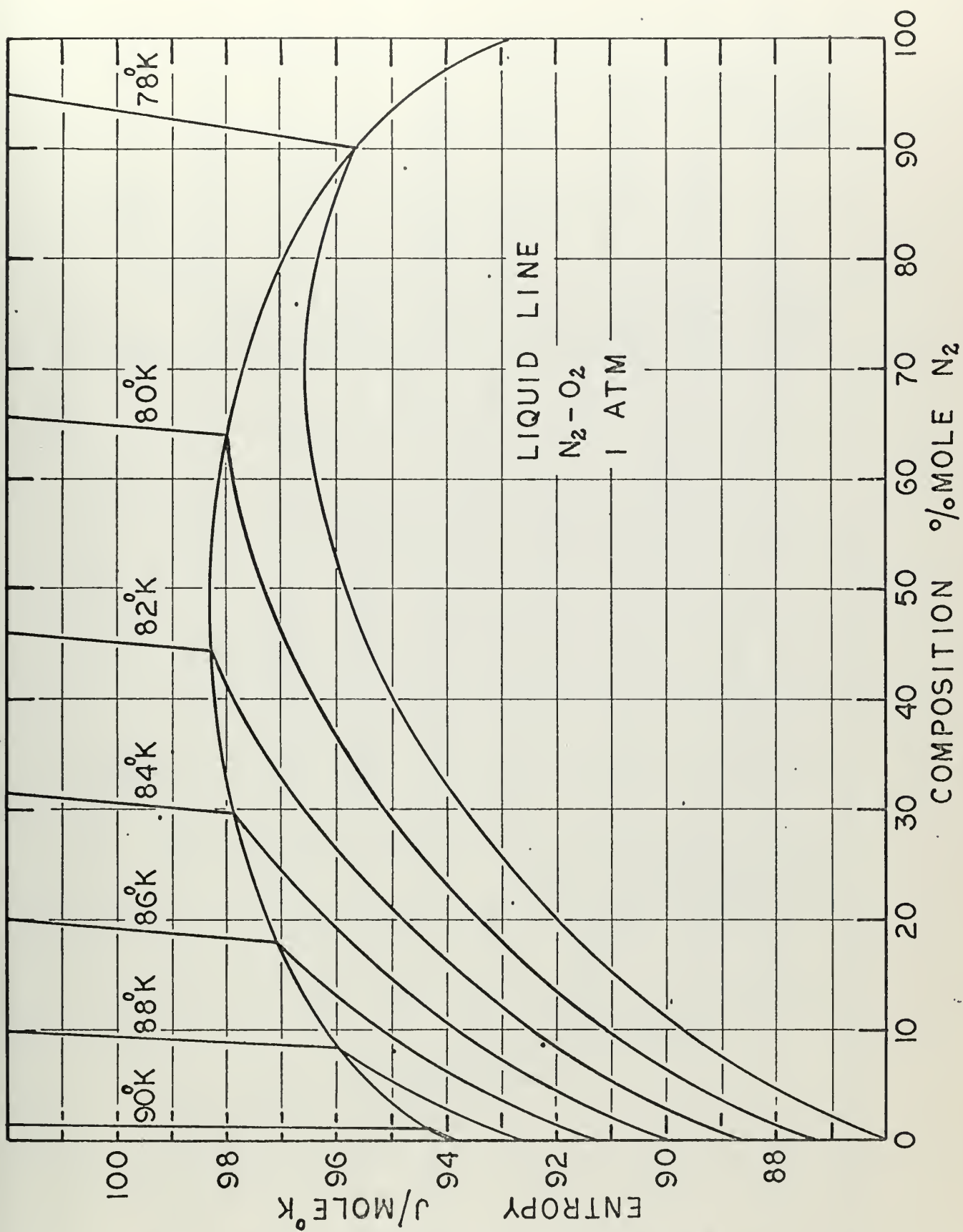
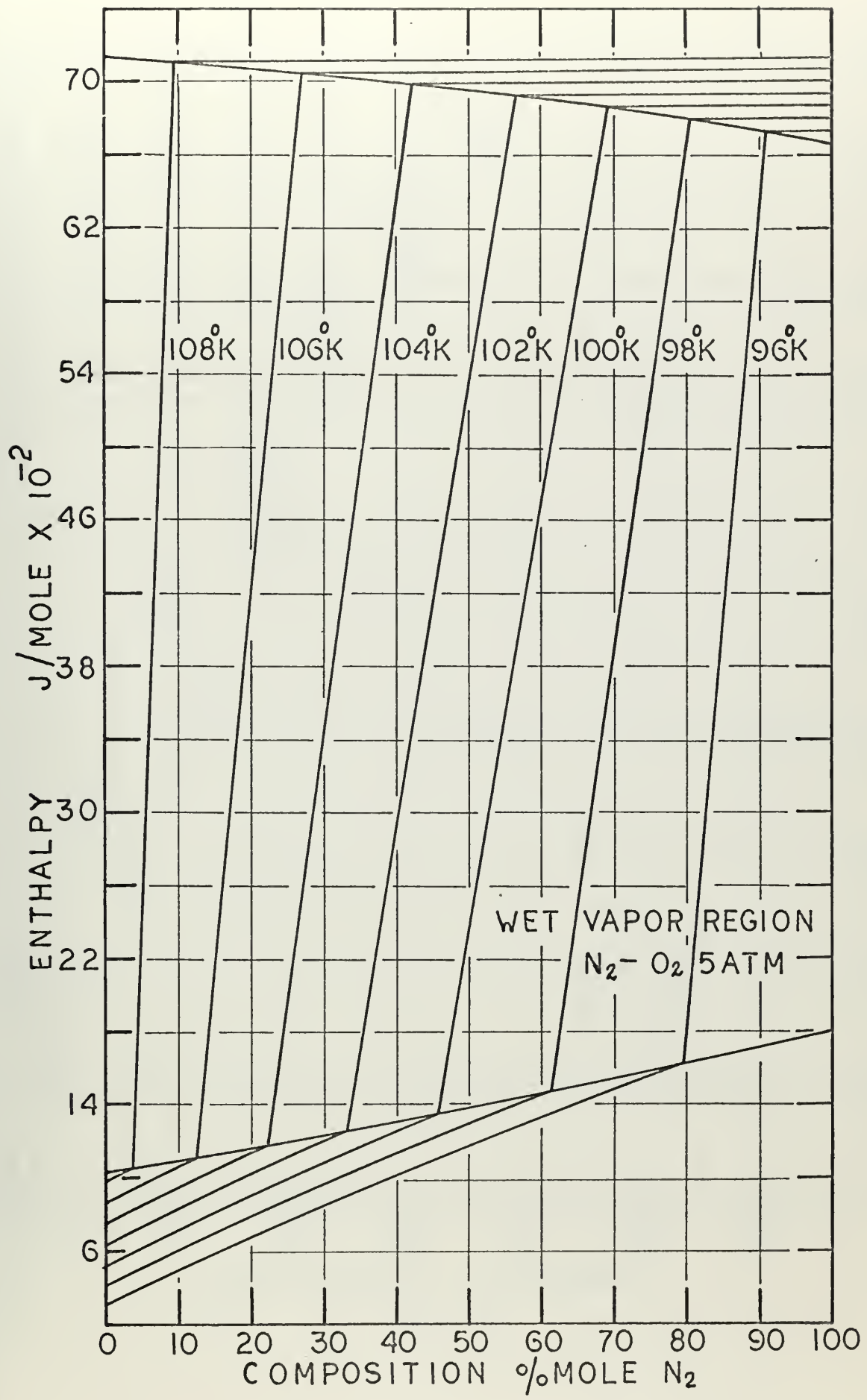


Figure 12

Figure 13



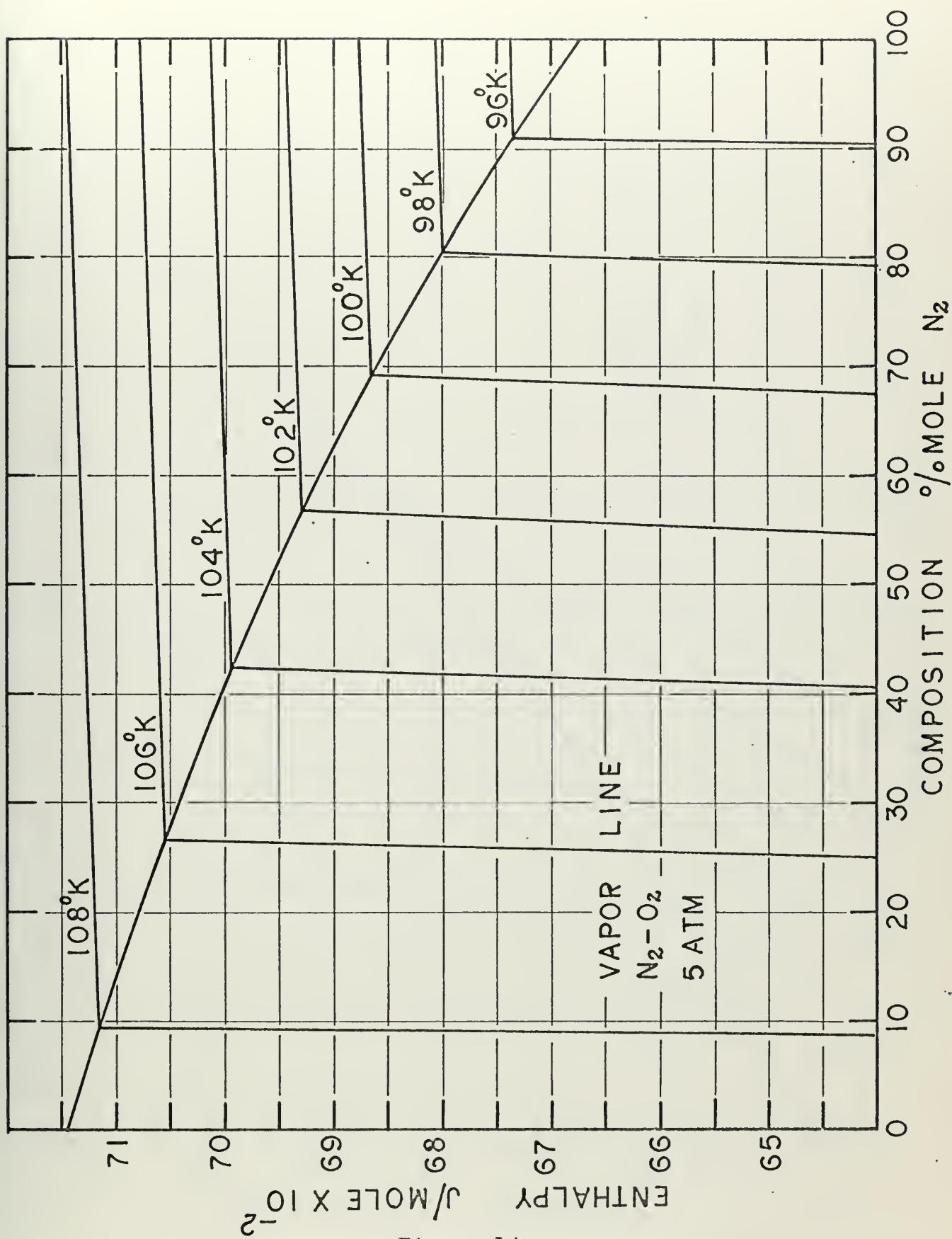


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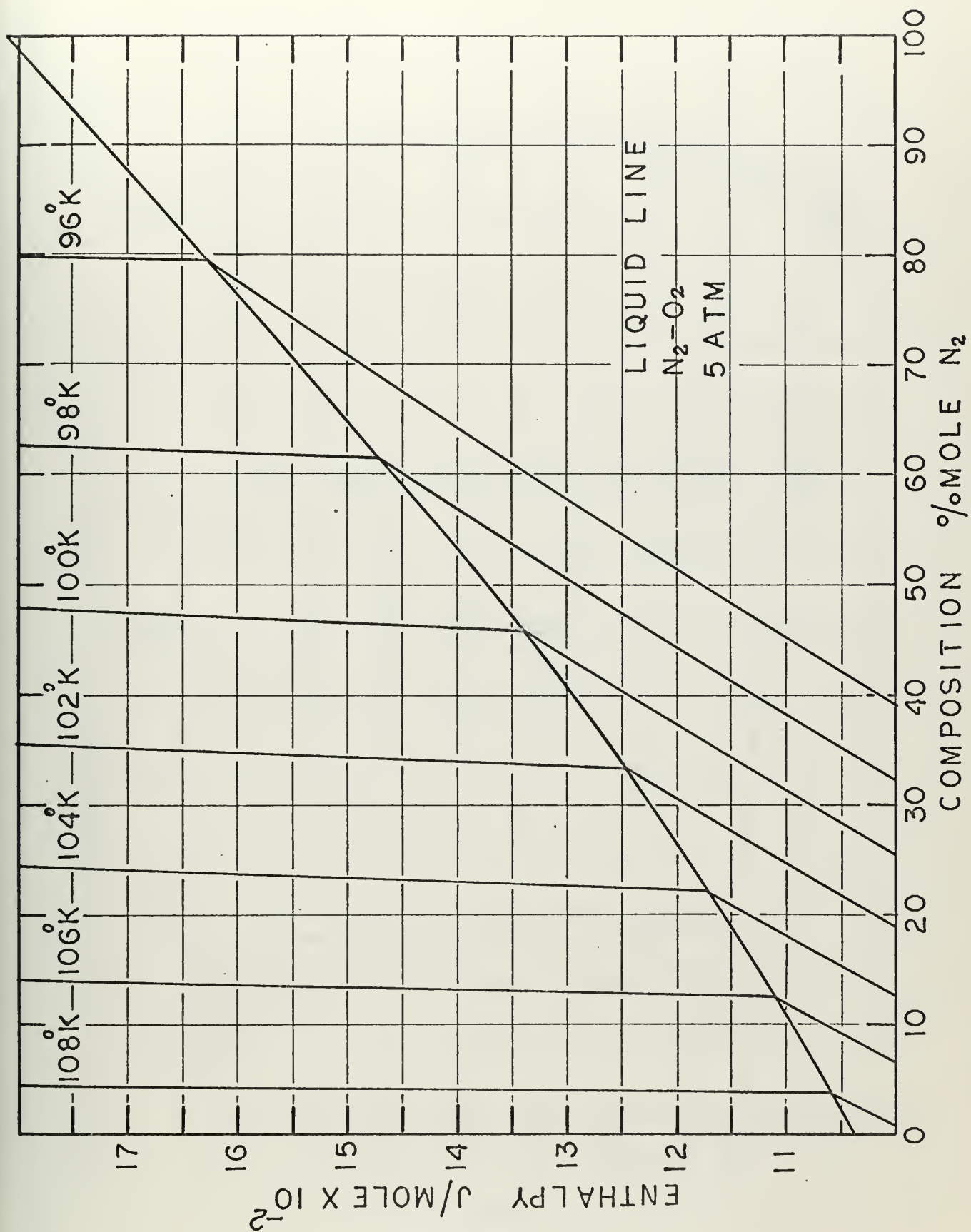


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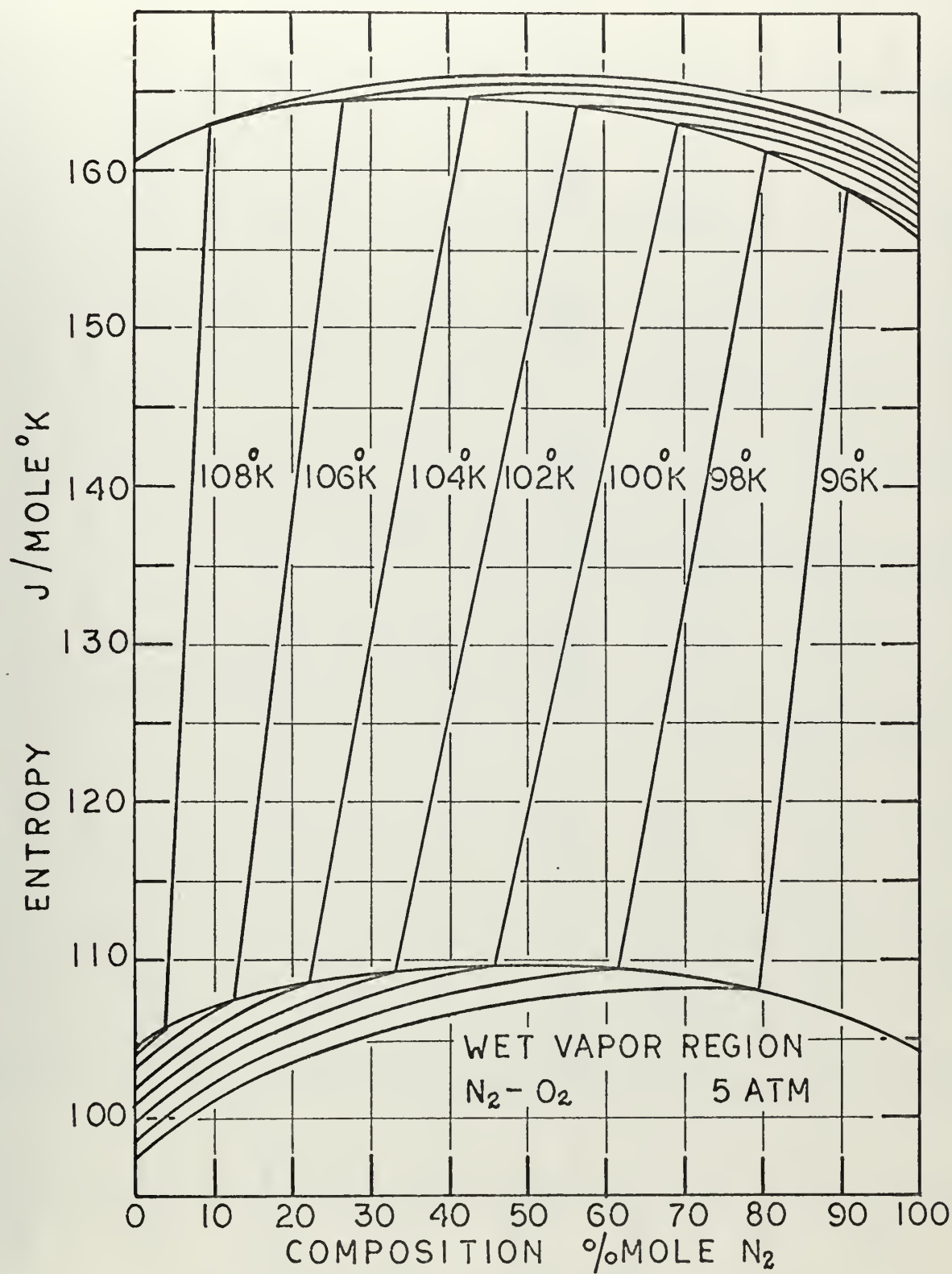


Figure 16

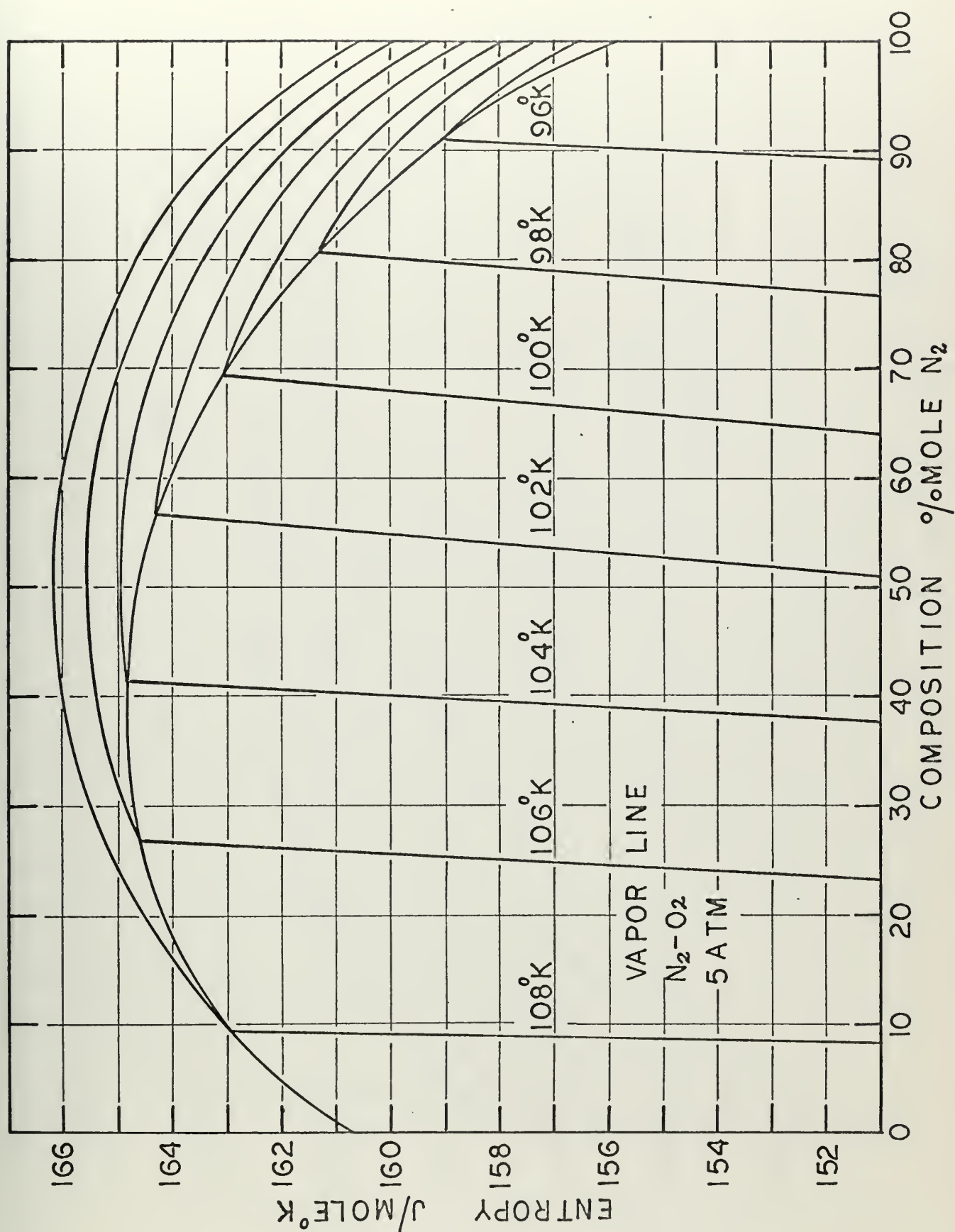


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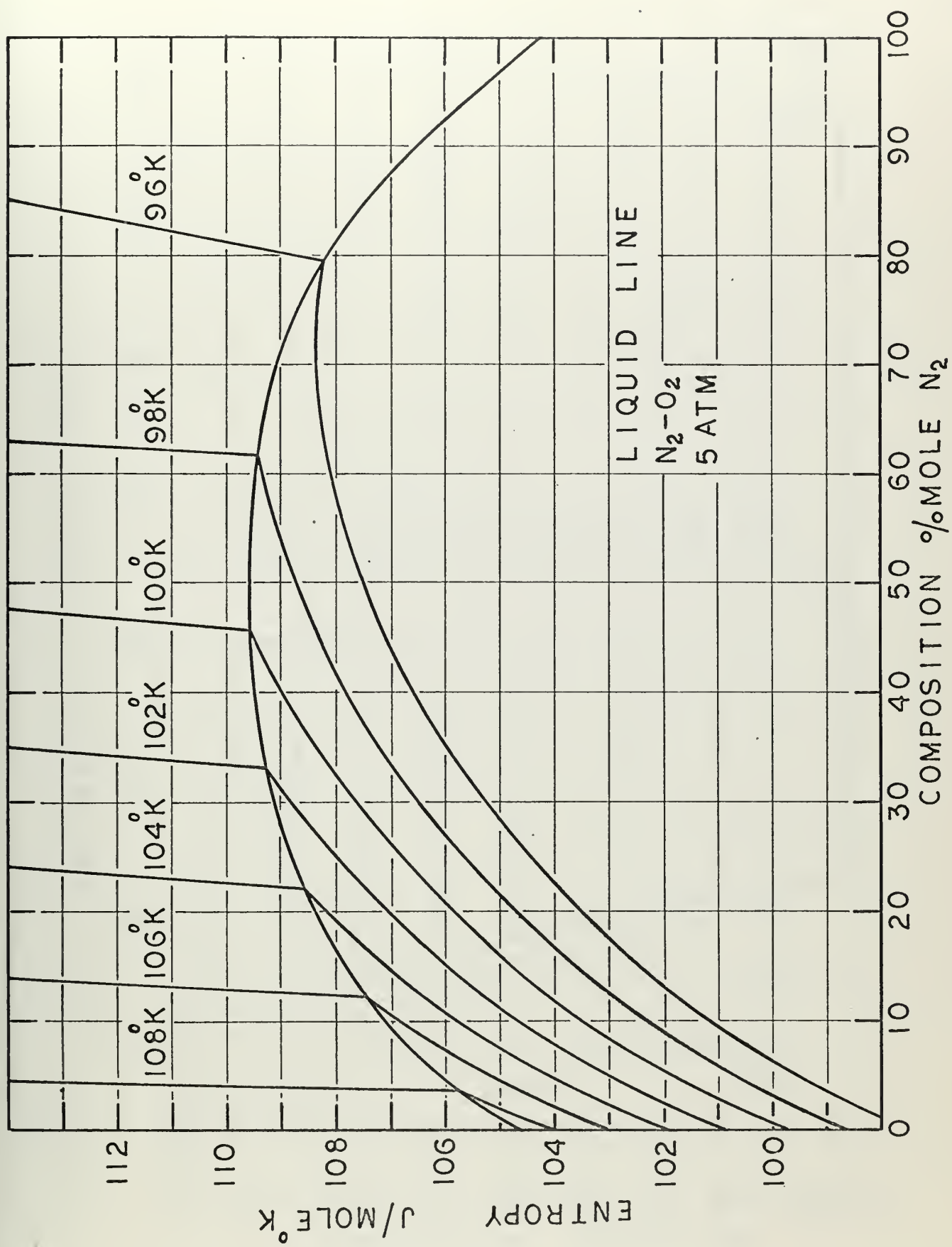


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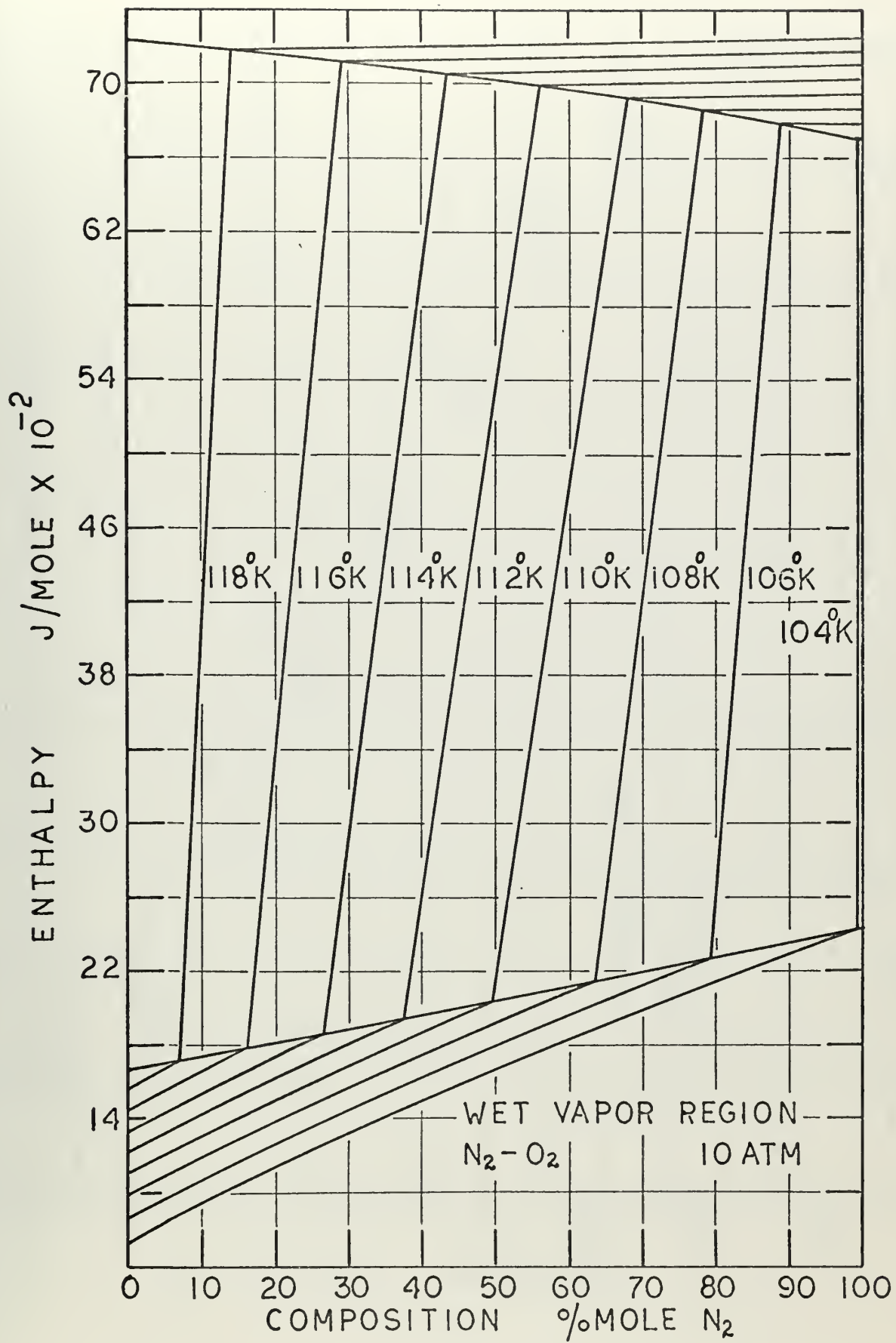


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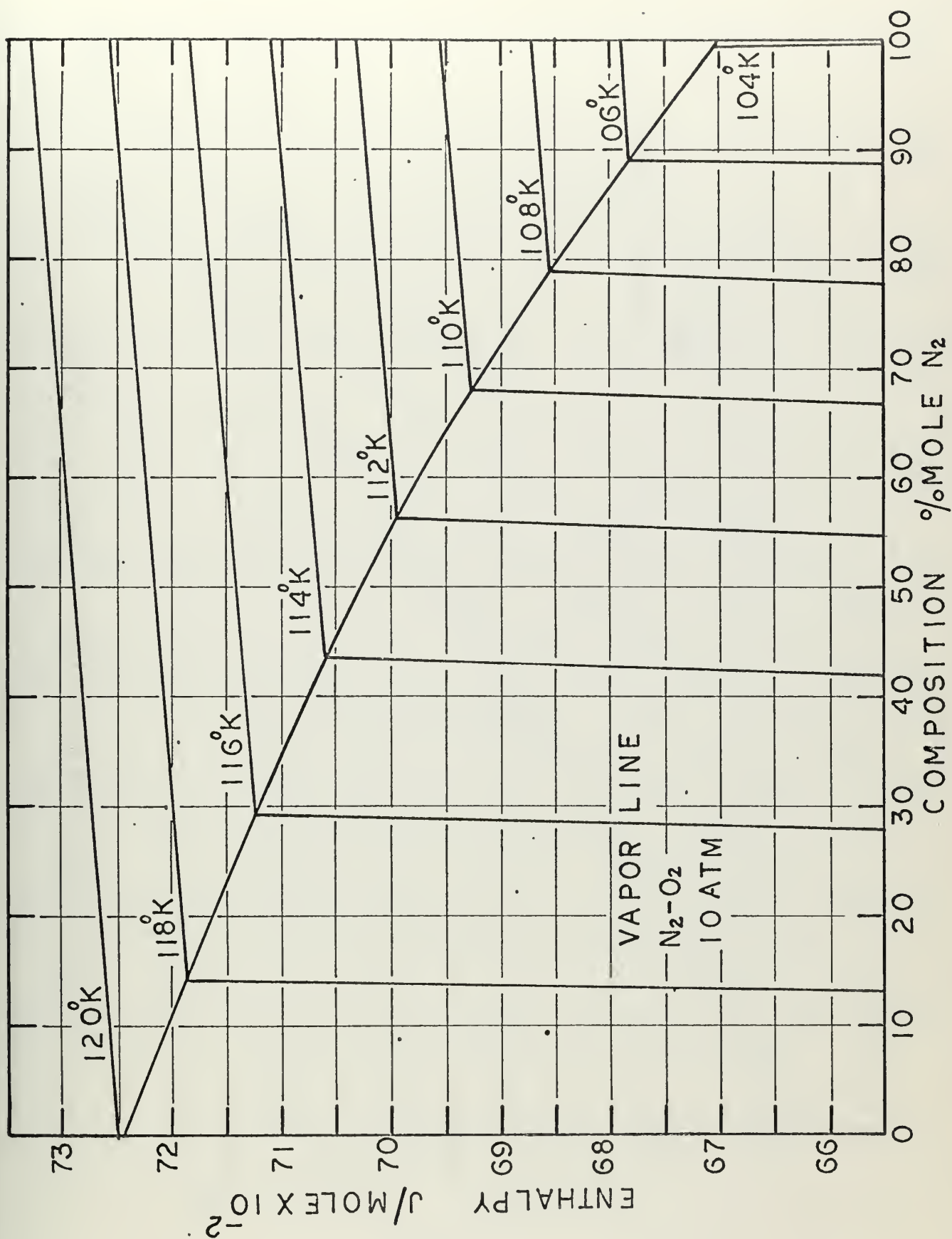


Figure 20

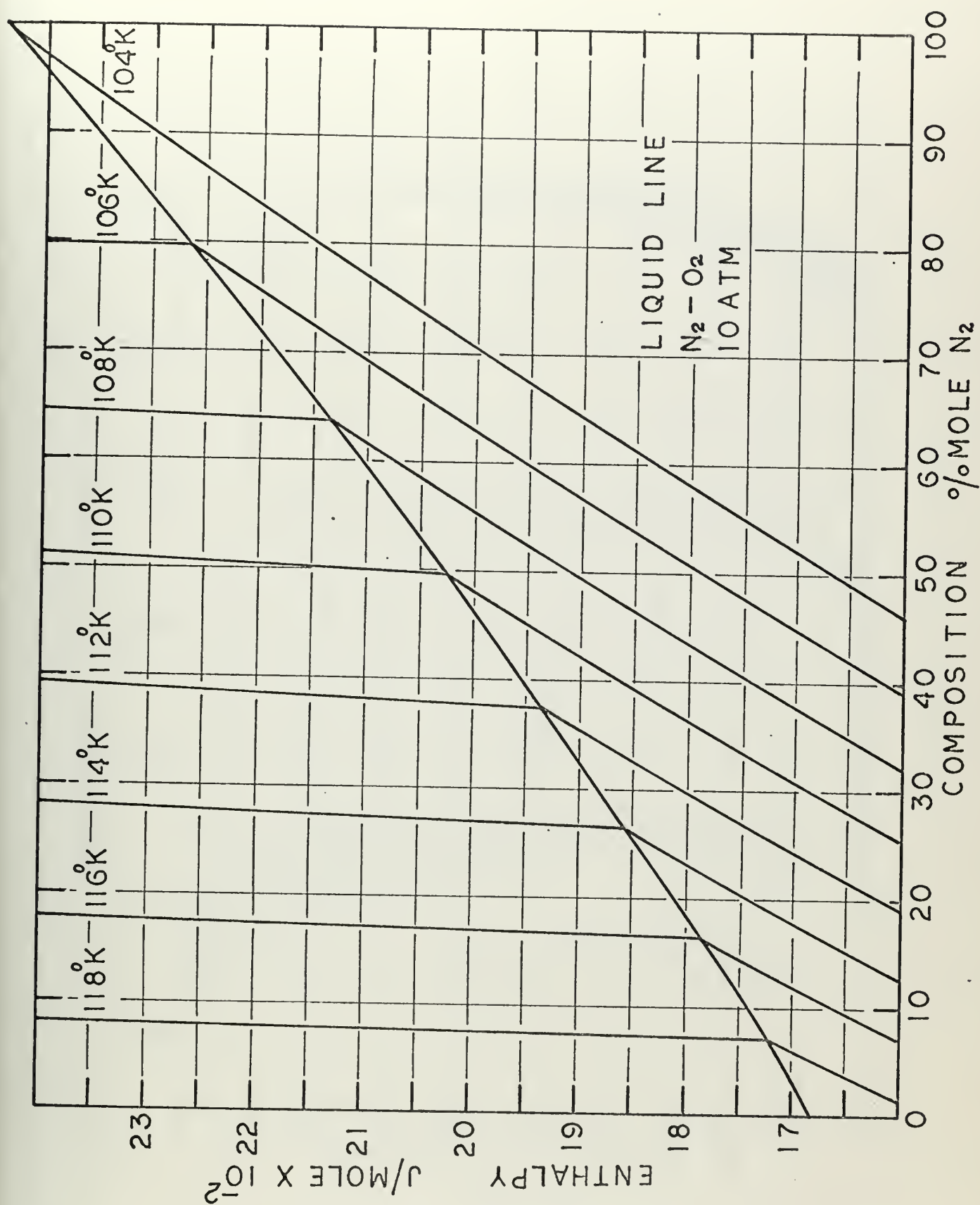


Figure 21

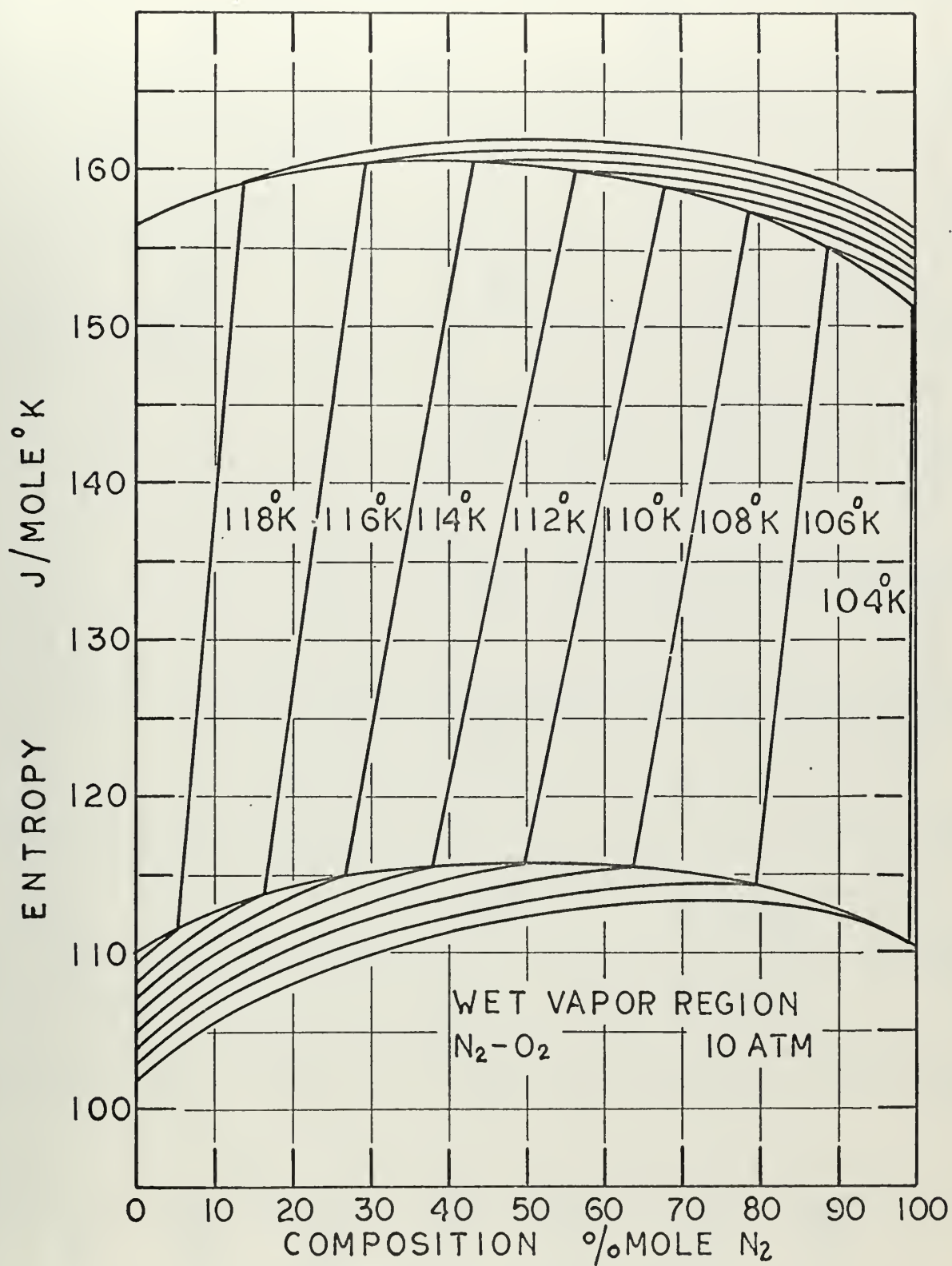


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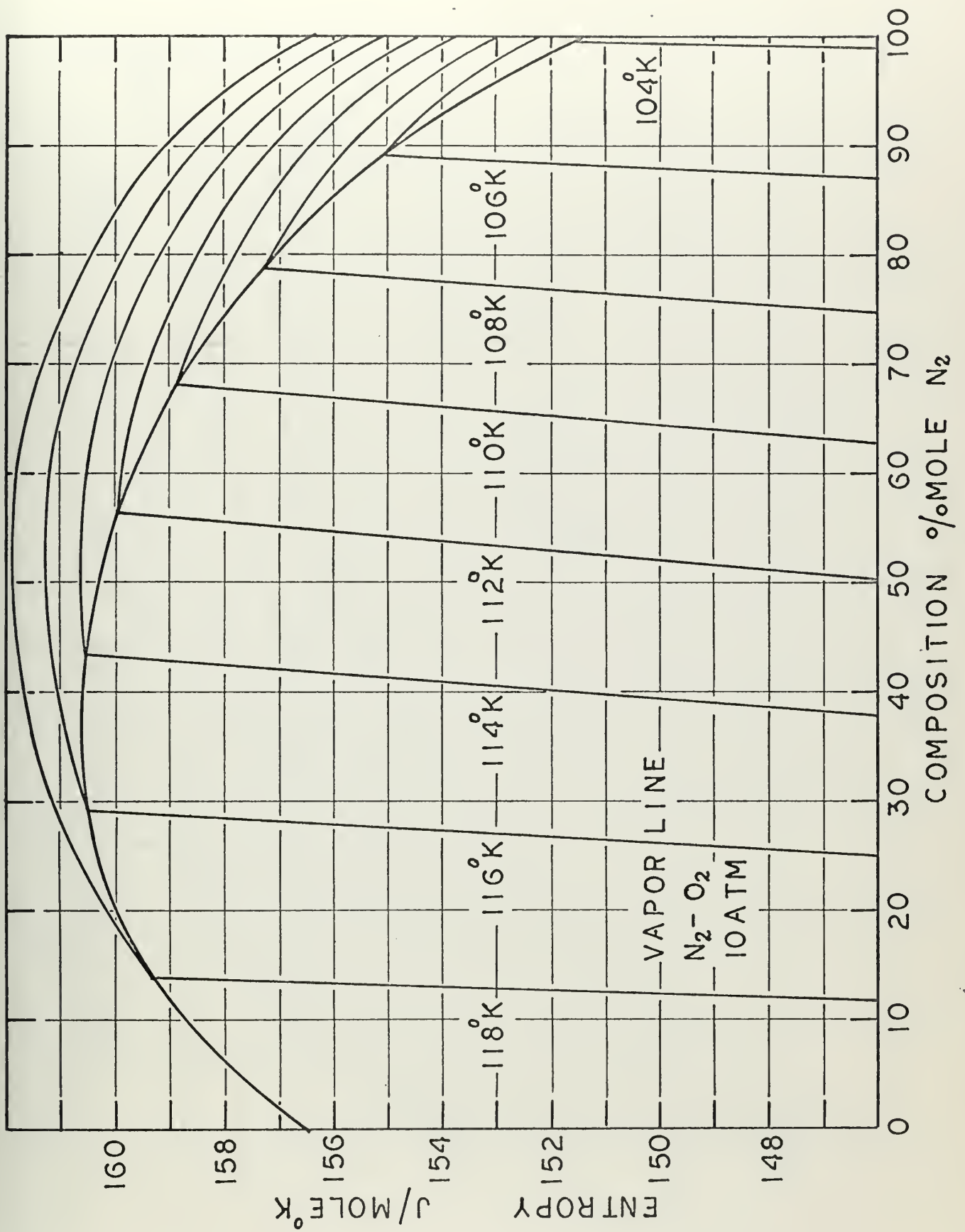


Figure 23

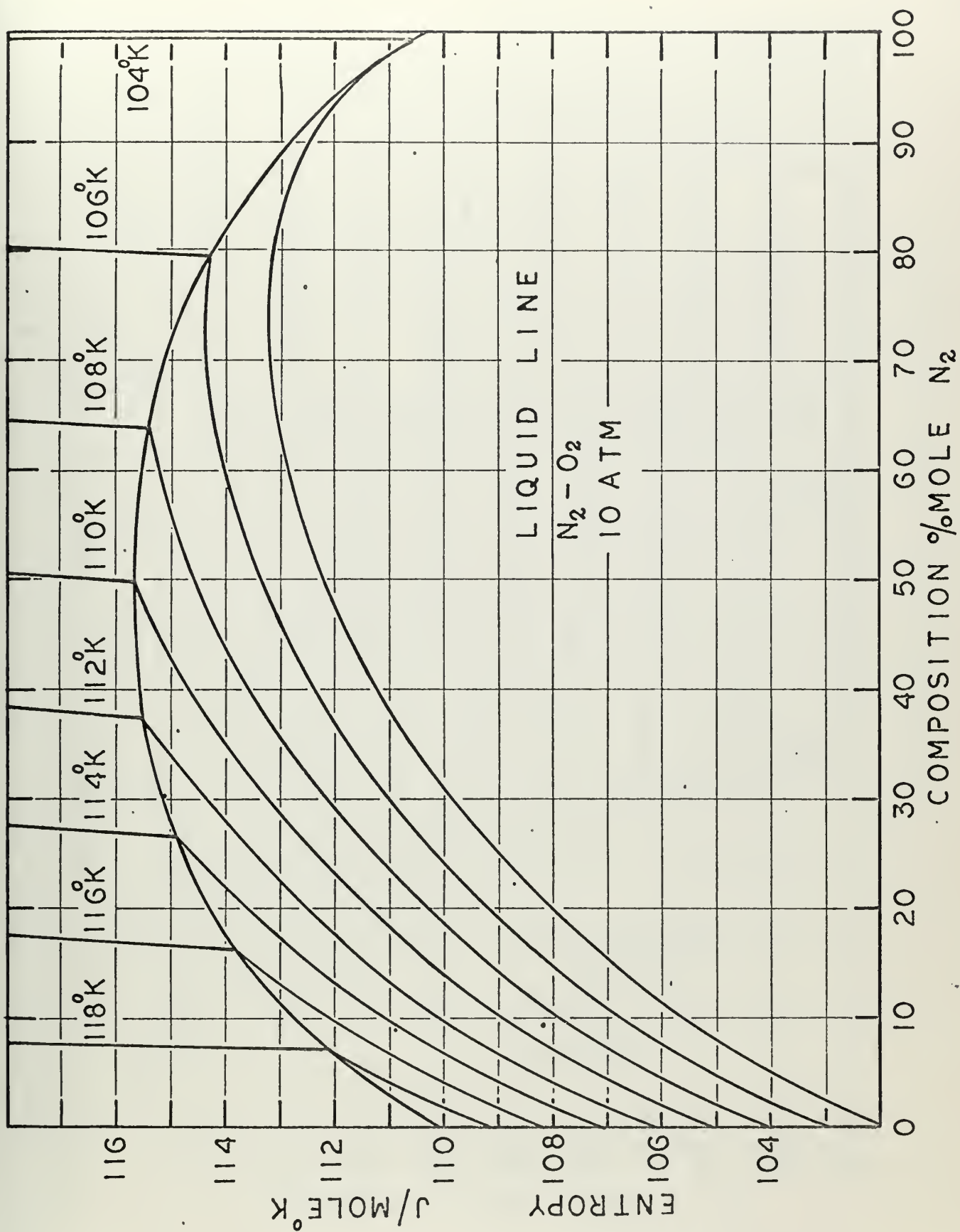


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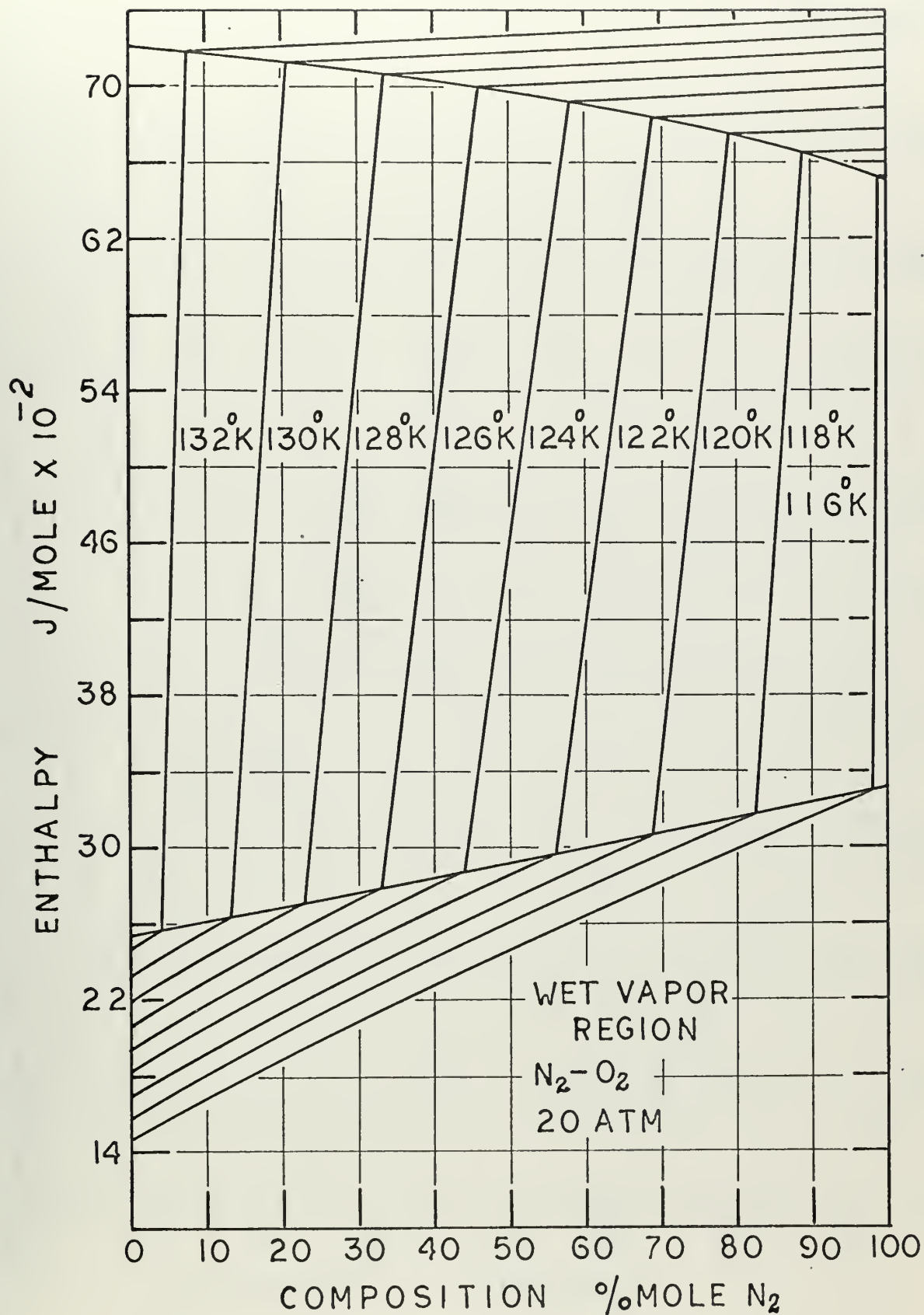


Figure 25

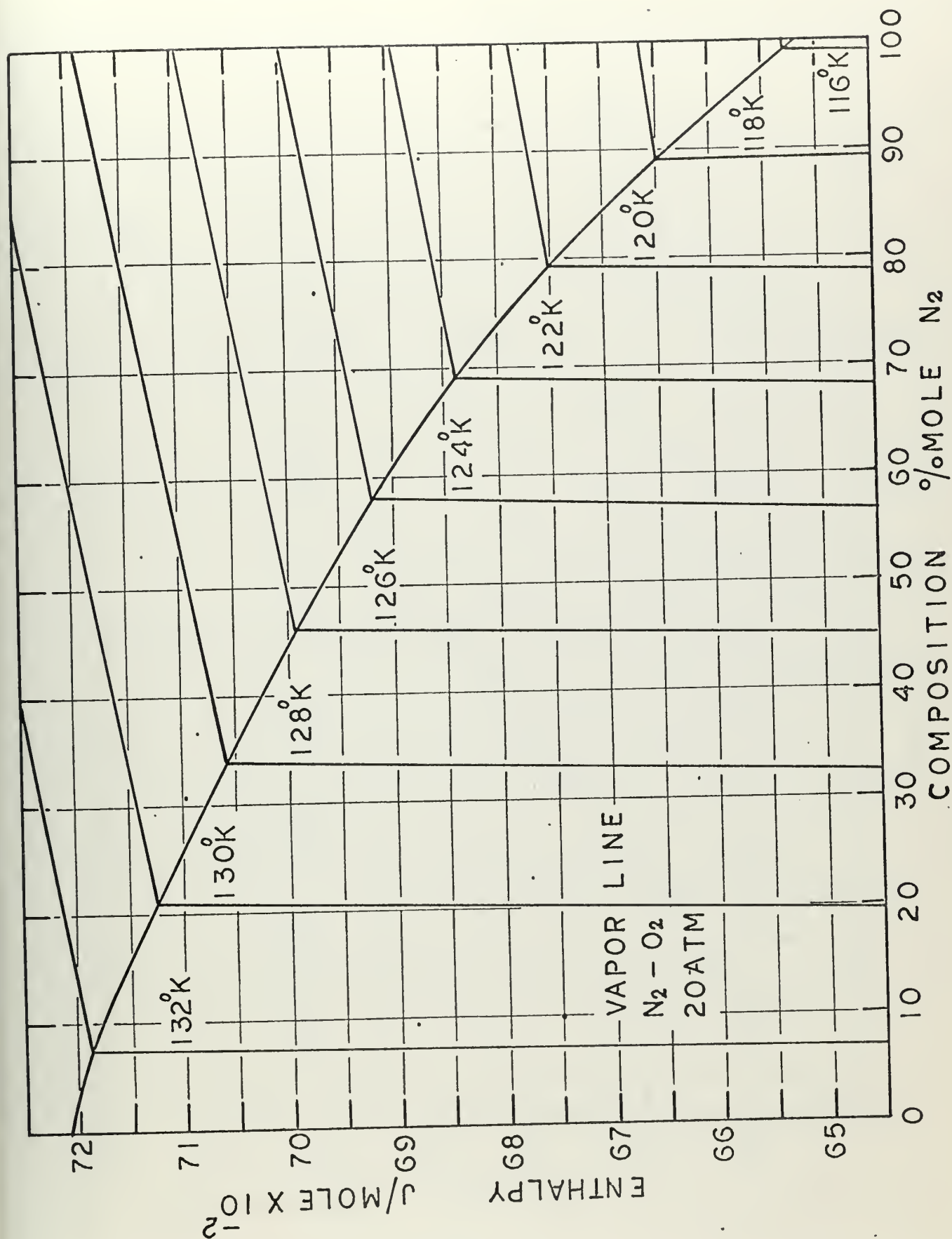


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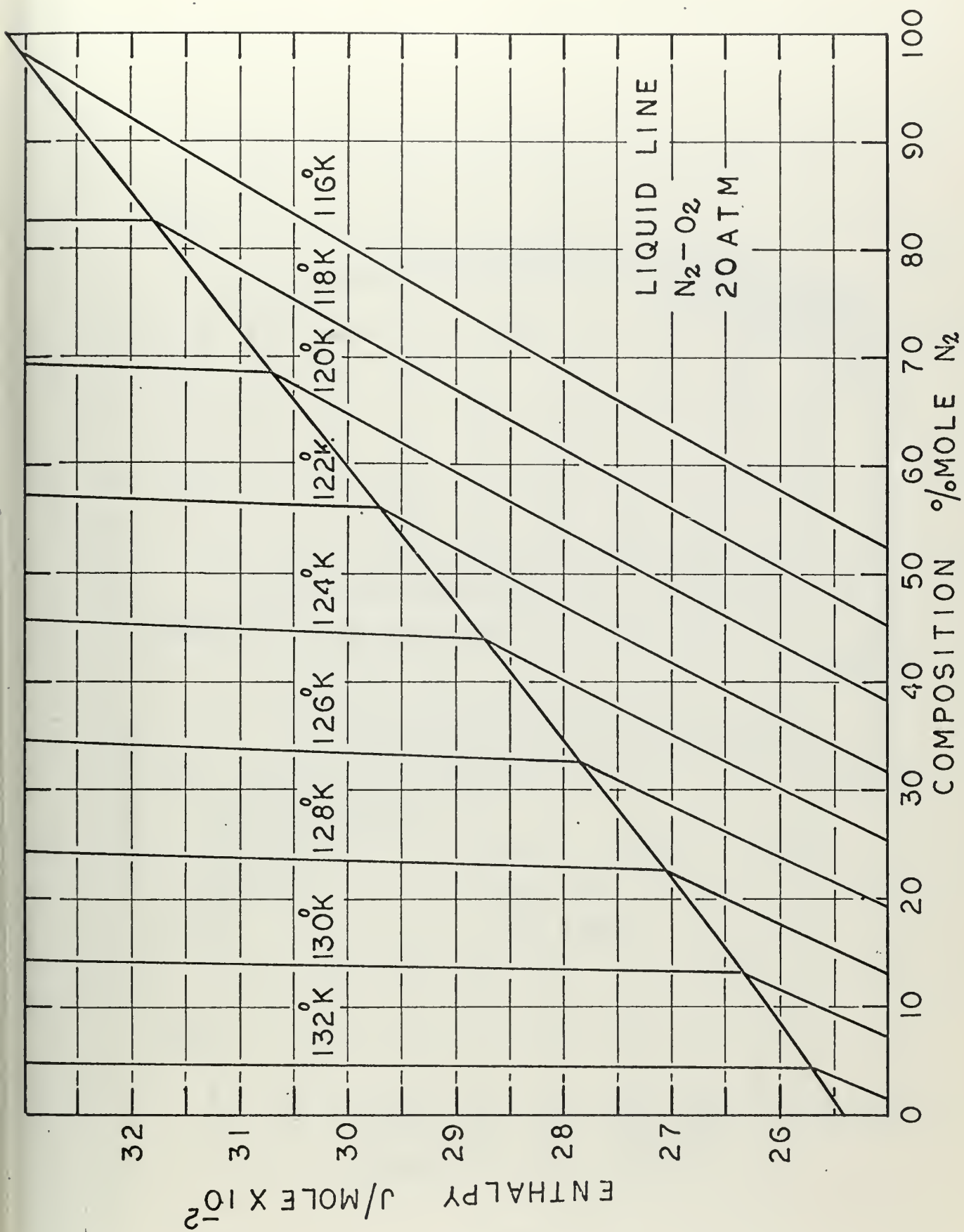


Figure 27

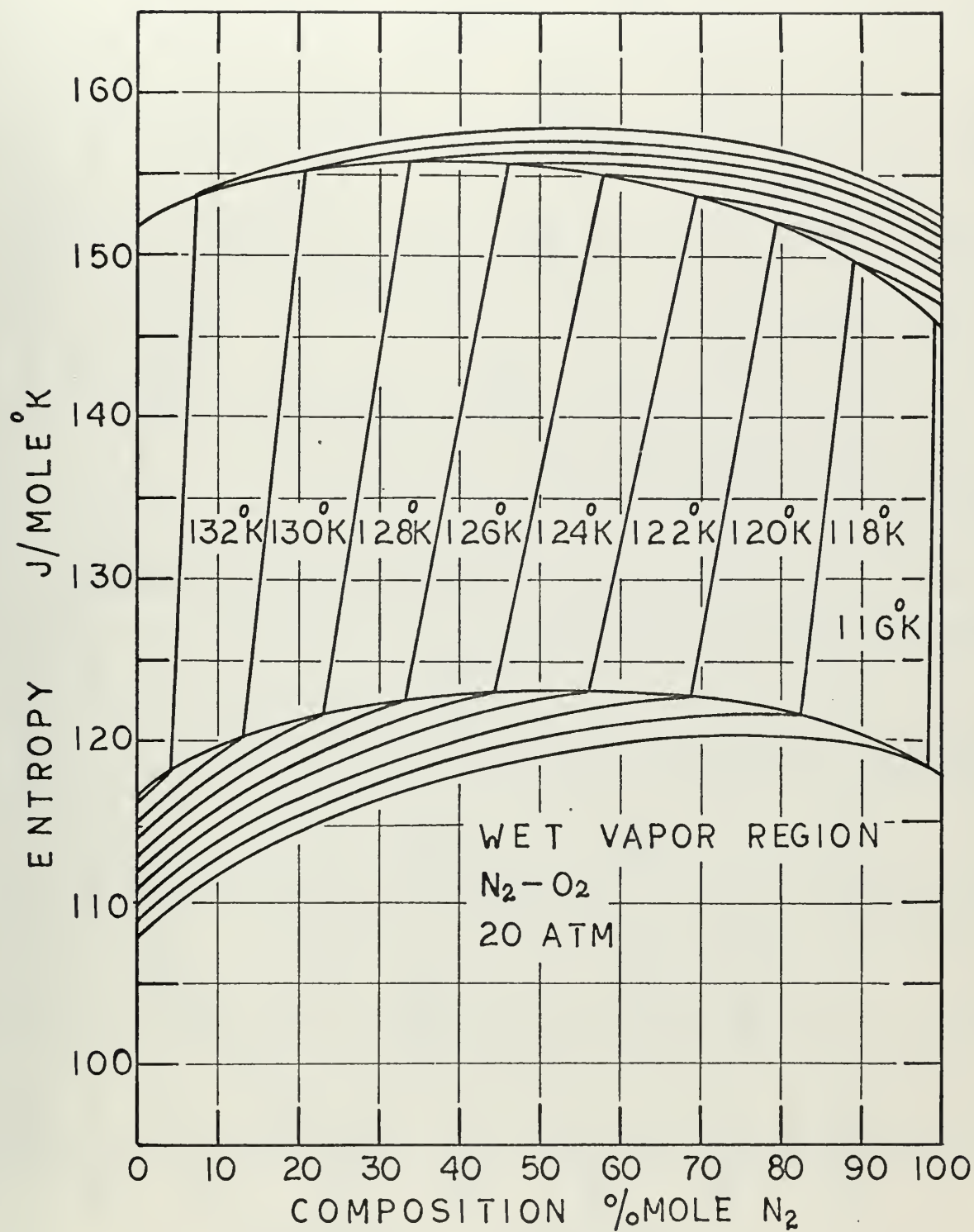


Figure 28

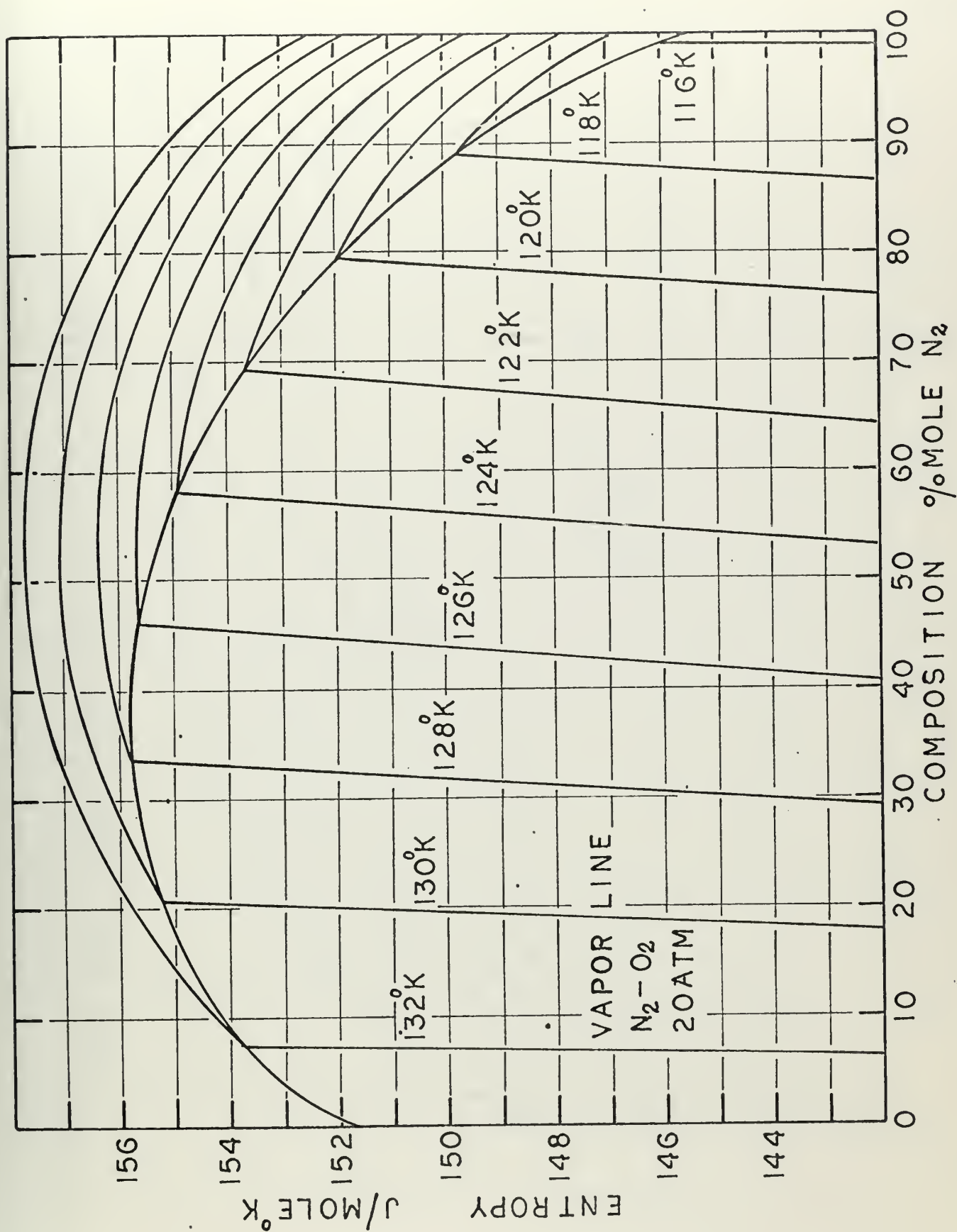


Figure 29

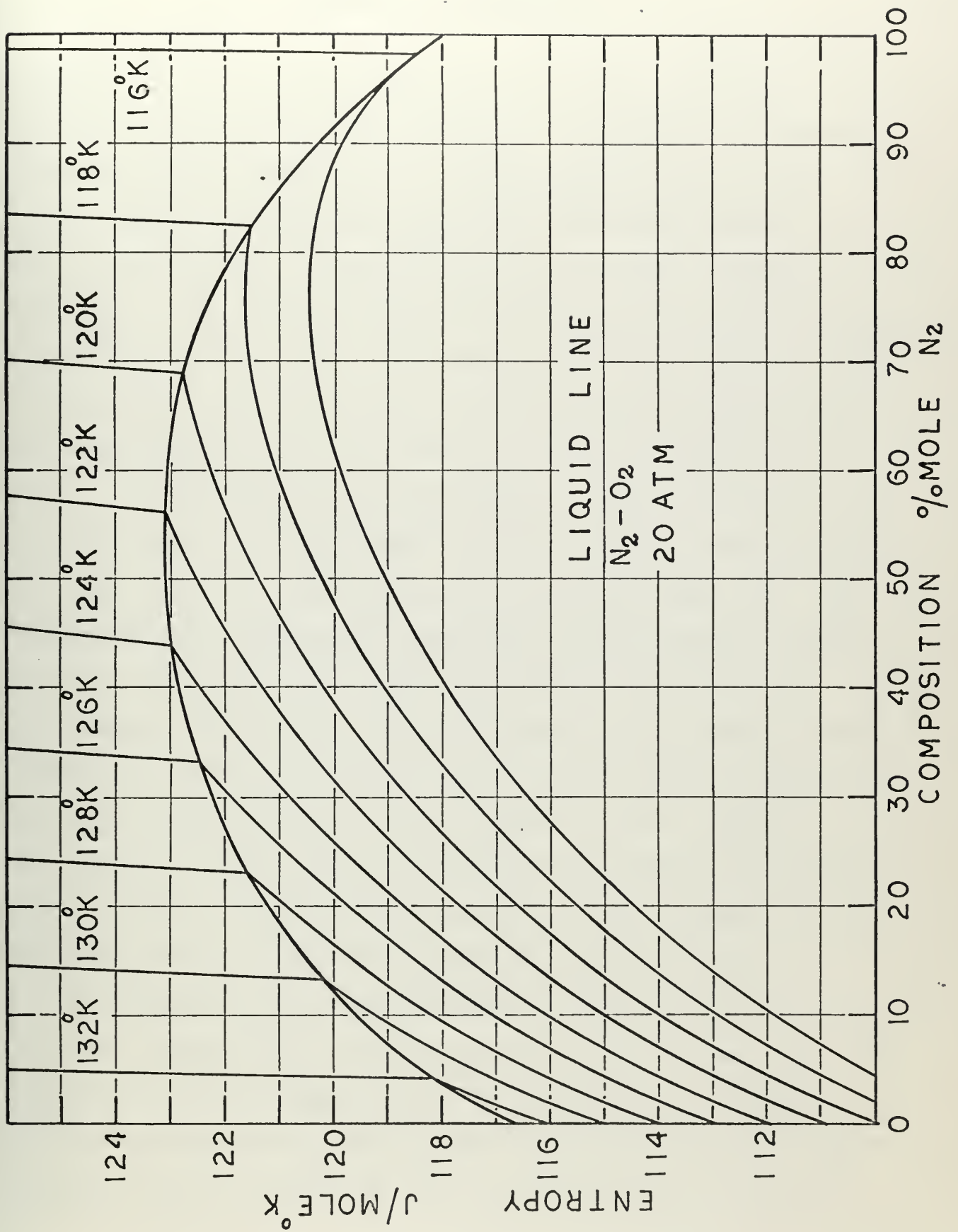


Figure 30

DISCUSSION OF RESULTS

The choice of the method of determination and the form of presentation of the results was arrived at after consideration of all the previously discussed techniques. No attempt was made to formulate a virial expansion or other empirical equation of state, because of a general lack of the PVT data required for such a formulation. A corresponding states theory estimation technique, using pseudocritical constants and the enthalpy deviation tables of Lydersen, was conducted, with the results already mentioned. The negative excess heats calculated by this method are thermodynamically inconsistent, and this procedure was rejected. Using pseudocritical constants, a modified relation for the latent heat was calculated, which when plotted produced the least agreeable of all liquid lines determined (Fig. 31). The purely graphical approach of Lerberghe produced better results, except at high molar concentrations, which plotted extremely erratically. Both a mole fraction average of the heats of vaporization of the pure components and a mole fraction average of the pure component boiling points produced better results in that order, than did the complex estimation techniques mentioned above. A plot of the results obtained by these methods at 1 atm together with the method finally chosen is given in Fig. 31.

In the end it was decided that the calculation of excess functions provided the best determination of the liquid line, and therefore of the isotherms in the liquid region. The liquid line determined by this method shows very good correlation with the experimental evidence of Dana, as can be seen in Fig. 31.

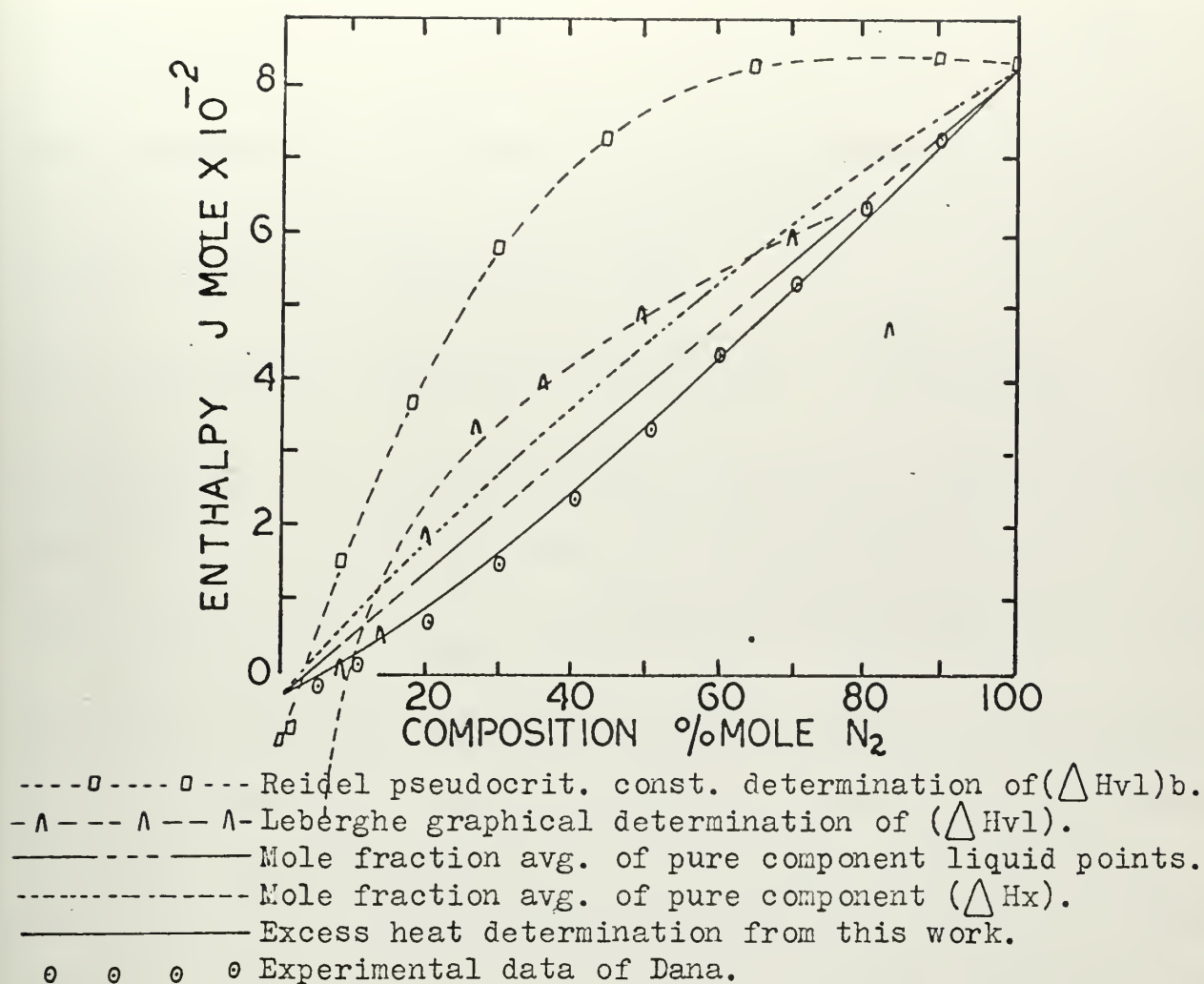


Figure 31. Liquid line for N_2 - O_2 mixtures at atmospheric pressure.

A presentation of the excess Gibbs free energy as calculated by previous investigators is shown in Fig. 32. The excess Gibbs free energy is related to the other excess functions by

$$H^E = G^E + TS^E = G^E - T \left(\partial G^E / \partial T \right)_P \quad (46)$$

It is clear from Fig. 32 that the slope of G^E with respect to temperature is very linear in the low pressure region and has been measured as 0.08 cal/mole $^{\circ}K$. With this slope the excess heat of the liquid was calculated to be 16.0 cal/mole at equimolar

composition and low pressure. Only one experimental calculation of excess heat for N_2 - O_2 liquid mixtures has ever been made [1]. These measurements by Knobler et al of the excess heat at $77^\circ K$ are plotted as Fig. 33. These results can be expressed by the fitted polynomial approximation [2].

$$H^E = x_{N_2} x_{O_2} [42 + 10(2x_{O_2} - 1) + 20(2x_{O_2} - 1)^2] \text{ cal/mole} \quad (64)$$

which yields an excess heat of 10.5 cal/mole at $x=0.5$. A concurrent calculation of G^E was made and can be given by

$$G^E = x_{N_2} x_{O_2} [40 + 4(2x_{O_2} - 1) + 4(2x_{O_2} - 1)^2] \text{ cal/mole.} \quad (65)$$

This gives an excess Gibbs free energy of 10.0 cal/mole at $x=0.5$ or a value nearly the same as that of the excess enthalpy. Since the temperature derivative of G^E is negative, then $H^E > G^E$, and from the weight of evidence by considerably more than 0.5 cal/mole. It was decided that 16.0 cal/mole was a reasonable value for the excess heat at equimolar composition in keeping with Fig. 32, and the good fit obtained in plotting the liquid line; Knobler's data was then scaled up to this result. It should be noted that in agreement with prediction [3] the excess heat is asymmetric with respect to the composition, while the curve of excess free energy is symmetrical. Values of the excess entropy were then calculated from Eq. (46).

When the calculated values of excess heat were applied to isotherms in the liquid region at one atmosphere, the resulting liquid line showed excellent agreement with the experimental data of Dana. It was decided, therefore, that this technique

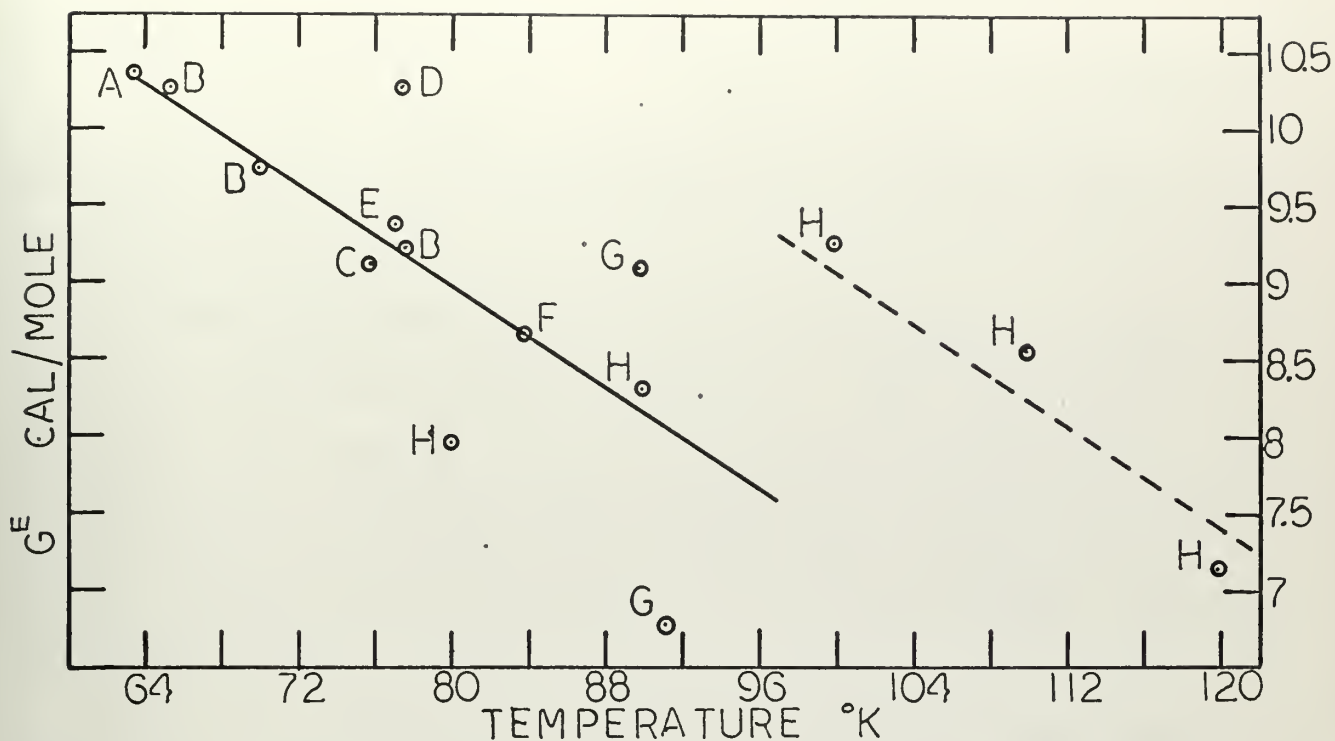


Figure 32. Excess Gibbs free energy as a function of temperature for equimolar liquid mixtures of N_2 - O_2 . See Appendix C for data sources.

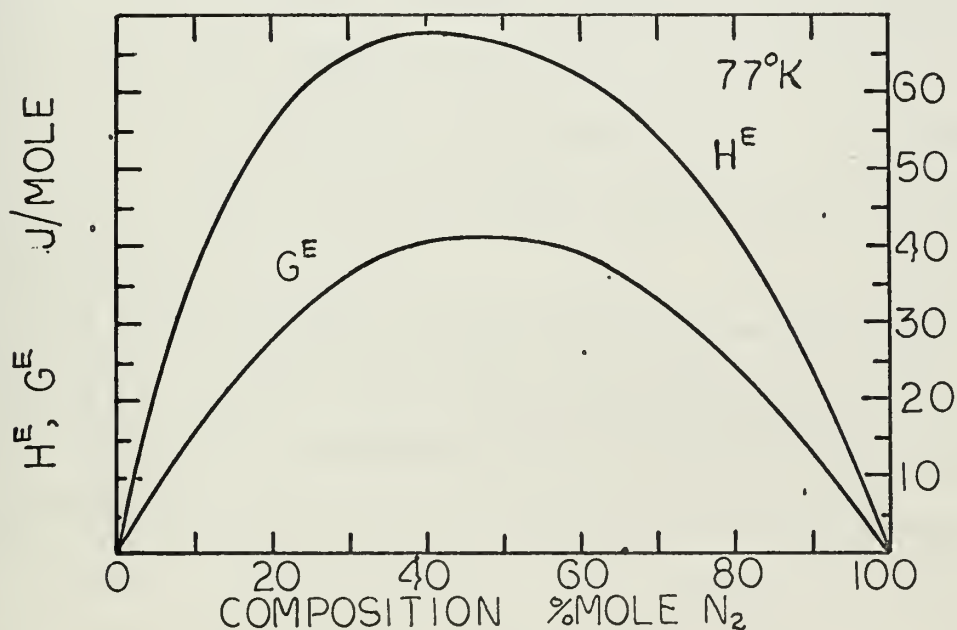


Figure 33. Excess heat and excess Gibbs free energy as a function of composition from the data of Knobler et al. H^E fitted to revised equimolar value of this thesis.

at atmospheric pressure was the best available.

The integration method of Bosnjakovic was used to calculate $(S^V - S^L)_x$. The liquid line thus determined for the S-x diagram was in excellent agreement with that calculated from values of the excess entropy.

In the vapor phase it had been decided that most authors generally agreed that there was negligible heat involved with mixing at low pressures including atmospheric, so that the best approximation of isotherms was a simple mole fraction average corresponding to the mixing rules for an ideal mixture; this includes the entropy of mixing for the S-x diagram vapor line.

The major problem then, concerned pressures greater than atmospheric, that strangely ignored and abandoned region where investigators have feared to tread. It would be foolhardy and certainly not justifiable to make unwarranted assumptions about conditions at higher temperatures where pressures exceed several atmospheres, where the third virial coefficient, the compressibility of the liquid, and the volume change on mixing are all important factors.

For the best available presentation it was decided that the excess functions of heat and entropy already calculated would be used to determine the isotherms of the liquid and mole fraction averaging the vapor isotherms at pressures and temperatures below the critical. This decision is not wholly without justification. It is not unreasonable to assume that the excess thermodynamic properties of the liquid are relatively independent of pressure [4], principally because of the relatively small volume changes in the liquid state. Additionally, Fig. 32 gives some

small hint that deviations at the higher temperatures associated with the higher vapor pressures are not so great from the more accurately calculated linear results at lower temperatures.

The incompressibility reasoning does not apply so well in the dense gas region, but here too it is felt that the ideality of mixture assumption is valid enough when compared to other available data. The values of several investigators for air [5,6,7,8] were compared at the pressures in question at several isotherms near the dew point and compared to the 79% mole N_2 mixture of nitrogen and oxygen isotherms calculated by mole fraction averaging. Although the deviations varied widely, a positive excess heat with increasing pressure might seem to be indicated, the effects of argon in the mixture and the particular investigations notwithstanding. The deviations are not large enough nor their pattern clear enough to justify guesswork at possible values of excess heat.

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CONCLUSIONS

The intention of this thesis was to survey the literature with regard to the thermodynamic properties of binary mixtures of nitrogen and oxygen in the two-phase region and to analyze the resulting data. From the sizeable collection of available printed matter which concerns itself directly and indirectly with the subject, it would seem an easy matter to make an analytical determination of the common thermodynamic properties of such relatively simple mixtures. A wide variety of estimation techniques do, in fact, exist, and while those have been presented here, most, if not all, of them are either unsatisfactory or at least only partially useful.

Specifically, the virial expansion and other equations of state with their associated derivatives would be most satisfactory if experimental PVT data existed with which to determine their coefficients. Molecular theory, similarly, has great potential, particularly for liquids and dense gases, but suffers from the uncertainty involved in its basic parameters. The techniques involving pseudocritical constants give good rough estimates, but do not provide the accuracy required for even engineering calculations. The excess functions provide a rapid and relatively easy method for determining the thermodynamic properties. Presently available data on these give good results at pressures near atmospheric.

All of the aforementioned methods have one thing in common. None of them have been developed for use in the high pressure

area of the two-phase region. Where no one has gone before, however, any determination, no matter how simplified, idealized, or approximated it may be, is better than none at all. Therefore it was decided that by taking the excess functions independent of pressure in the liquid region and using ideal mixture rules in the vapor phase, satisfactory thermodynamic diagrams could be constructed.

RECOMMENDATIONS

Under this heading of Recommendations should be listed the solutions to the problems posed by the Results. At the risk of redundancy and speaking only for the mixtures in question these inadequacies are repeated here.

A single equation of state for all mixtures would be the most satisfactory solution as it would provide in one analytical expression and its derivatives the measureable and derived properties for the infinite number of mixtures. A solution of this type would require an extensive experimental program to determine a sufficient number of PVT data to permit the evaluation of appropriate coefficients.

Another satisfactory program would be to make direct measurements of the excess heat function using one of the calorimeters mentioned previously. This is the only satisfactory means of determining this property and at high pressure the only means. Then since the vapor pressure method of determining G^E is only satisfactory at essentially atmospheric pressure, the excess entropy function could be determined by the integration procedure

discussed earlier under Graphical Methods. A program of this type would not be all inclusive in its results and would necessitate taking measurements at sufficiently close intervals of temperature to permit reasonable interpolation of tabulated data or accurate drafting of thermodynamic diagrams.

APPENDIXESAppendix A

1. Temperature-composition diagram, 1 atm.
2. Temperature-composition diagram, 5 atm.
3. Temperature-composition diagram, 10 atm.
4. Temperature-composition diagram, 20 atm.

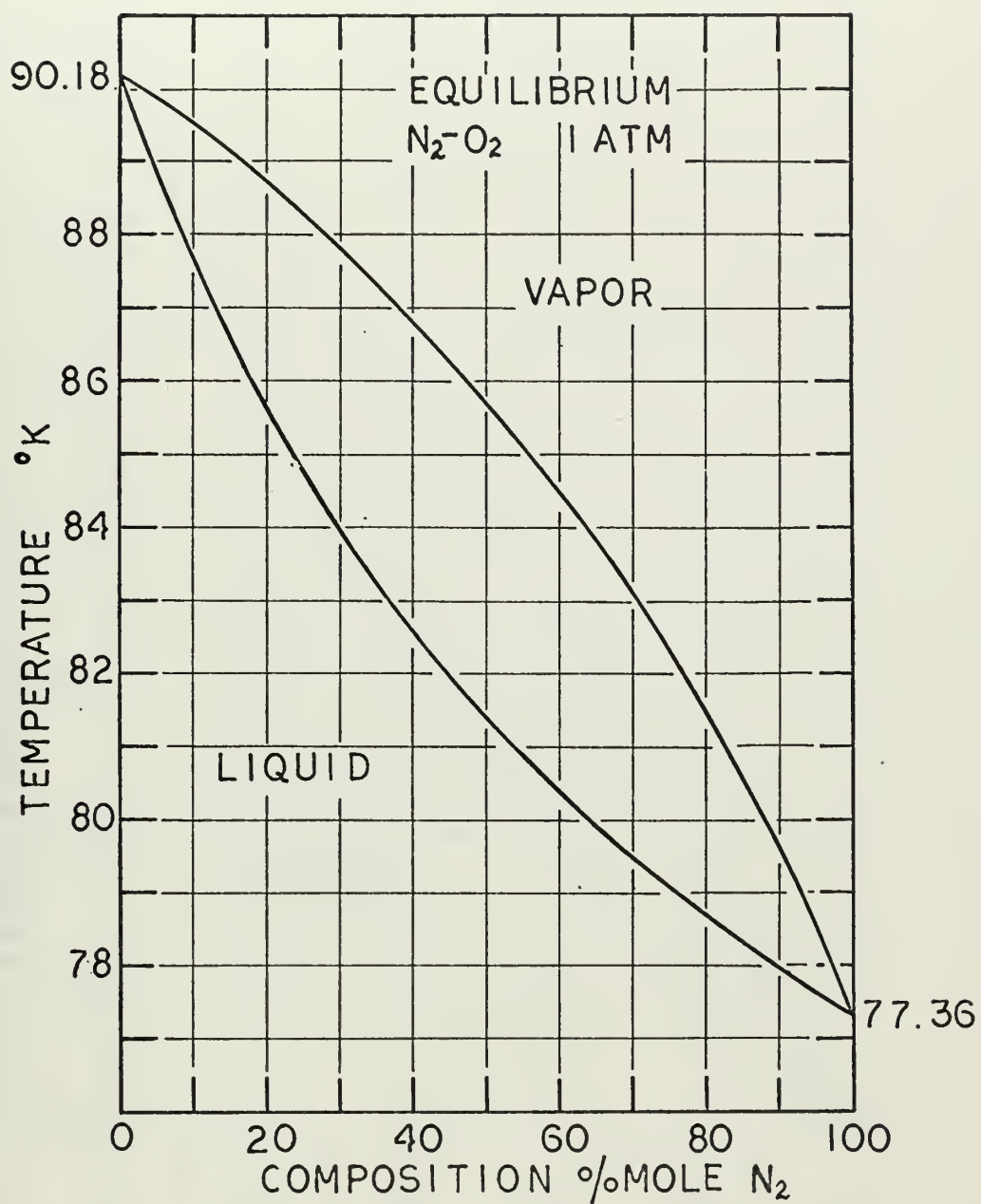


Figure 34

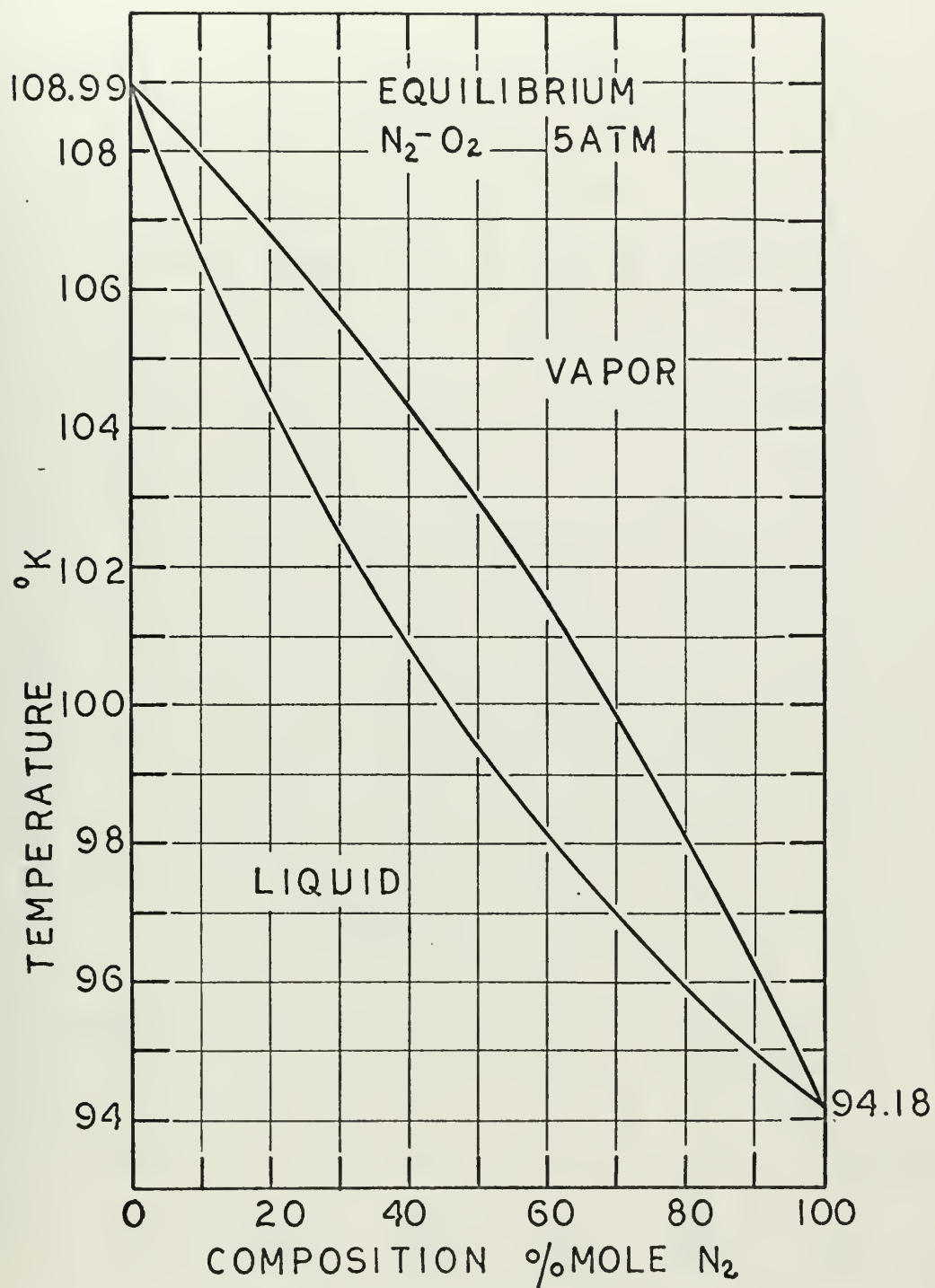


Figure 35

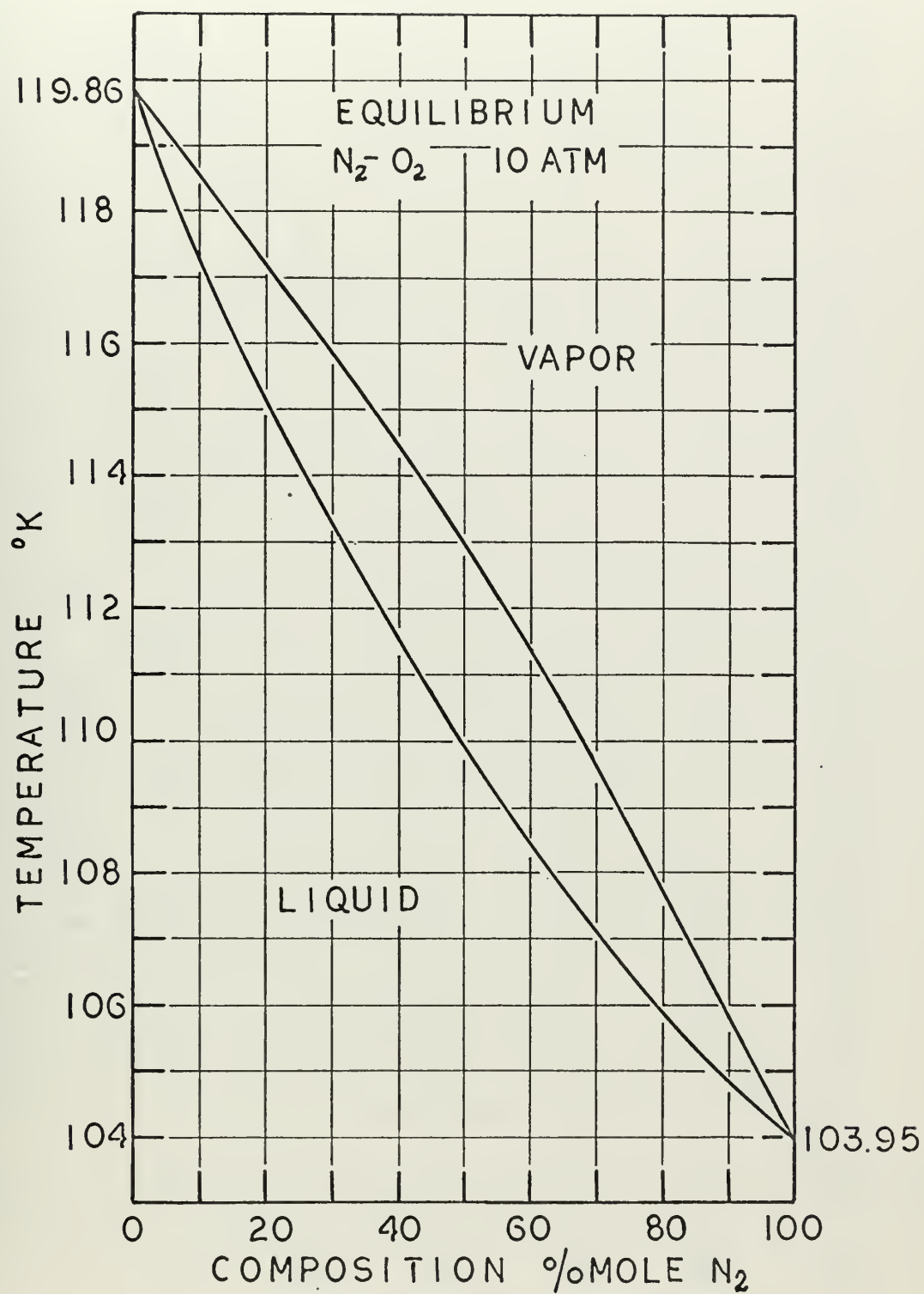


Figure 36

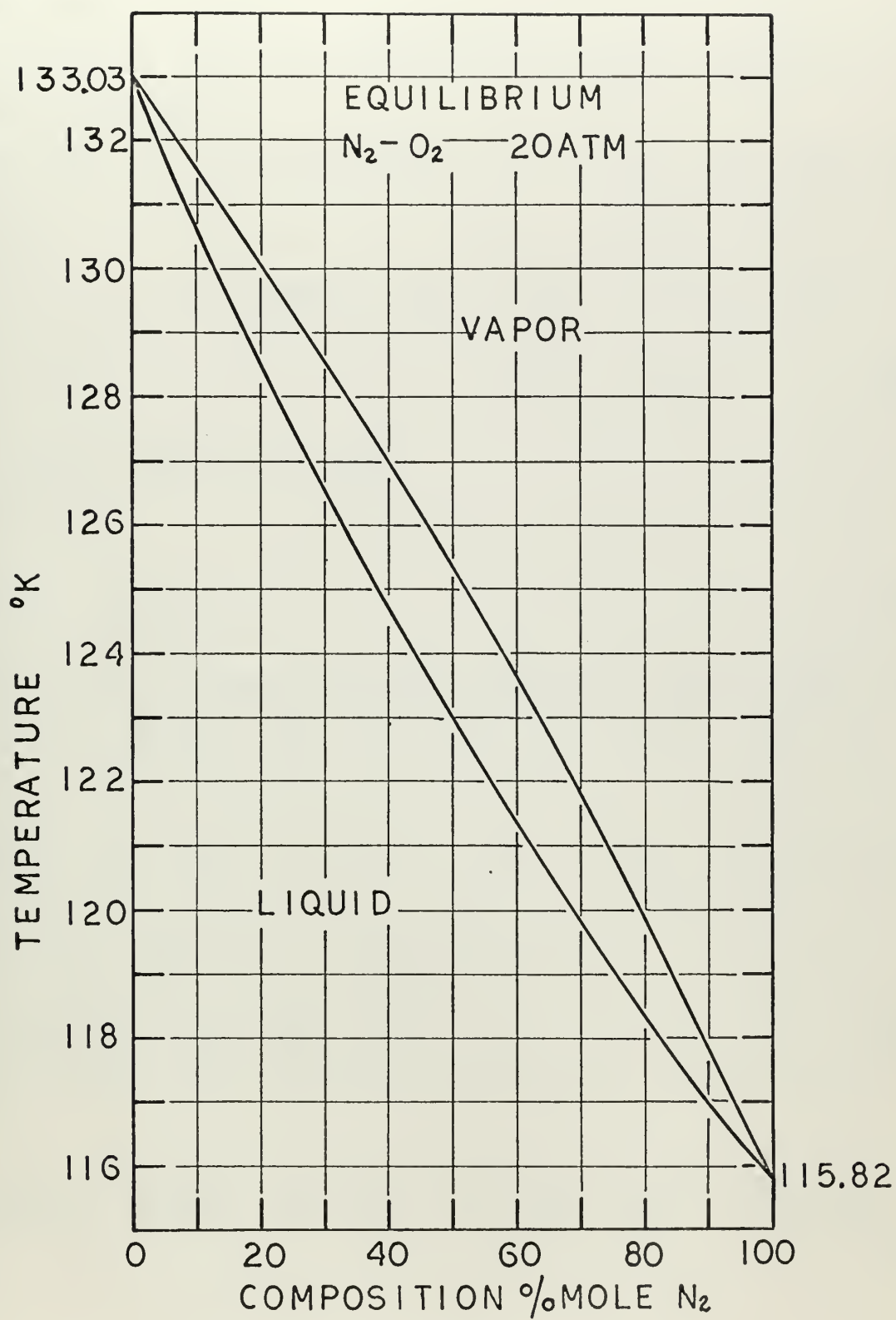


Figure 37

APPENDIX B

Barker's method:

The most widely noted method of determining G^E from measured isothermal values of total vapor pressure and liquid composition is that set out by Barker.

The excess chemical potential is given by Eq. (47) which can be written

$$\begin{aligned} \mu_{N_2}^E = RT \ln N_2 = RT \ln(Px_{N_2}^v/P_{N_2}x_{N_2}^l) + (V_{N_2}^l - B_{N_2})(P_{N_2} - P) \\ + P\delta_{N_2O_2}(x_{O_2}^v)^2 \end{aligned} \quad (66)$$

with a similar equation for $\mu_{O_2}^E$.

It follows that

$$P = \gamma_{N_2}\bar{P}_{N_2} + \gamma_{O_2}\bar{P}_{O_2} \quad (67)$$

where \bar{P}_{N_2} and \bar{P}_{O_2} represent partial pressures if the liquid is an ideal solution but the vapor is a non ideal mixture. They are given by

$$\bar{P}_{N_2} = x_{N_2}^l P_{N_2} \exp (V_{N_2}^l - B_{N_2})(P - P_{N_2})/RT - P \delta_{N_2O_2}(x_{O_2}^v)^2/RT \quad (68)$$

with a similar expression for \bar{P}_{O_2} and where

$$\delta_{N_2O_2} = 2B_{N_2O_2} - B_{N_2} - B_{O_2} \quad (69)$$

If

$$G^E = x_{N_2}^l \mu_{N_2}^E + x_{O_2}^l \mu_{O_2}^E = x_{N_2}^l x_{O_2}^l a + b(x_{N_2}^l x_{O_2}^l) + c(x_{N_2}^l - x_{O_2}^l)^2 \dots \quad (70)$$

then

$$\ln \gamma_{N_2} = A l_{N_2} + B m_{N_2} + C n_{N_2} \quad (71)$$

and similarly for $\ln \gamma_{O_2}$.

The values of l , m and n are expressed as

$$l_{N_2} = (x_{O_2}^1)^2, \quad l_{O_2} = (x_{N_2}^1)^2$$

$$m_{N_2} = -(x_{O_2}^1)^2(1 - 4x_{N_2}^1), \quad m_{O_2} = (x_{N_2}^1)^2(1 - 4x_{O_2}^1) \quad (72)$$

$$n_{N_2} = (x_{O_2}^1)^2(1 - 8x_{N_2}^1 + 12(x_{N_2}^1)^2) \quad n_{O_2} = (x_{N_2}^1)^2(1 - 8x_{O_2}^1 + 12(x_{O_2}^1)^2)$$

and $A = a/RT$, $B = b/RT$, $C = c/RT$.

As a first approximation the solution is assumed to be regular, such that $B=C=0$. By neglecting corrections for the vapor phase non ideality, A is set equal to $4\ln(2P_{x=.5}/P_{O_2} + P_{N_2})$.

\bar{P}_{N_2} and \bar{P}_{O_2} are then calculated for the various experimental liquid compositions from Eqs. (68). These are used to calculate γ_{O_2} , γ_{N_2} and P_{calc} from Eqs. (71) & (67) which in turn yield the pressure residual

$$R = P_{expt} - P_{calc} \quad (73)$$

and the derivatives

$$dP/dA = l_{N_2} \gamma_{N_2} \bar{P}_{N_2} + l_{O_2} \gamma_{O_2} \bar{P}_{O_2} \quad (74)$$

with similar expressions for dP/dB and dP/dC using m and n respectively.

Changes in A , B & C to most nearly reduce the pressure residuals to zero are determined by fitting by least squares to

$$(dP/dA) \delta A + (dP/dB) \delta B + (dP/dC) \delta C = R \quad (75)$$

or by solving simultaneously equations of the form

$$\delta_A \sum (dP/dA)^2 + \delta_B \sum (dP/dA)(dP/dB) + \delta_C \sum (dP/dA)(dP/dC) = \sum R(dP/dA) \quad (76)$$

with similar expressions for $\sum R(dP/dB)$ and $\sum R(dP/dC)$.

Appendix C

Selected Data

1. Equilibrium Data

P Atm	T °K	x ^l %mole N ₂	x ^v %mole N ₂	H ^l J/mole	H ^v J/mole	S ^l J/mole °K	S ^v J/mole °K
1	77.36	100	100	823.7	6793.5	92.84	165.00
	78	89.8	97.3	722.0	6790.0	95.62	166.23
	80	64.0	87.6	472.0	6727.0	98.00	169.18
	82	44.3	77.0	283.0	6666.0	98.27	171.28
	84	29.6	63.8	160.0	6607.0	97.88	173.05
	86	18.0	47.6	70.0	6547.0	97.08	174.00
	88	8.3	28.0	8.0	6486.0	95.95	173.88
	90	1.0	3.2	-29.0	6426.0	94.50	170.73
	90.18	0	0	-32.0	6406.1	93.94	169.63
5	94.18	100	100	1811.5	6672.3	104.21	155.84
	96	79.3	91.0	1630.0	6735.0	108.25	159.05
	98	61.3	80.4	1472.0	6800.0	109.49	161.33
	100	45.7	69.2	1337.0	6865.0	109.60	163.09
	102	33.0	56.7	1245.0	6928.0	109.28	164.32
	104	22.0	42.4	1171.0	6994.0	108.58	164.80
	106	12.3	26.6	1108.0	7053.0	107.45	164.58
	108	3.6	9.3	1057.0	7116.0	105.78	162.90
	108.99	0	0	1037.9	7144.7	104.60	160.63
10	103.95	100	100	2440.2	6702.3	110.34	151.36
	104	99.3	99.5	2433.0	6704.0	110.57	151.53
	106	79.3	89.0	2265.0	6783.0	114.27	155.12
	108	63.6	78.7	2137.0	6855.0	115.38	157.24
	110	49.6	68.0	2028.0	6926.0	115.65	158.88
	112	37.3	56.2	1939.0	6994.0	115.49	159.95
	114	26.3	43.4	1858.0	7060.0	114.89	160.55
	116	16.2	29.1	1784.0	7125.0	113.79	160.50
	118	6.9	13.8	1721.0	7186.0	112.12	159.30
	119.86	0	0	1681.7	7245.1	110.09	156.50
20	115.82	100	100	3321.9	6515.4	117.96	145.53
	116	98.2	99.0	3315.0	6529.0	118.48	146.00
	118	82.3	89.1	3177.0	6649.0	121.52	149.78
	120	68.8	79.4	3072.0	6752.0	122.79	151.98
	122	56.1	69.2	2972.0	6839.0	123.09	153.70
	124	44.1	58.0	2873.0	6919.0	122.98	154.91
	126	33.0	46.0	2785.0	6993.0	122.46	155.62
	128	22.8	33.7	2707.0	7058.0	121.53	155.77
	130	13.1	20.7	2631.0	7125.0	120.13	155.23
	132	4.1	7.3	2543.0	7190.0	118.13	153.77
	133.03	0	0	2542.0	7208.3	116.61	151.69

2. Pure Component Data

P Atm	T °K	H ₂ O J/mole	H ₂ N J/mole	S ₂ O J/mole °K	S ₂ N J/mole °K
1	65	-1347.1	108.4	76.95	82.77
	70	-1115.3	397.6	80.38	87.05
	75	-861.6	687.0	83.88	91.05
	80	-594.3	6486.3	87.32	166.02
	82	-485.3	6546.8	88.67	166.77
	84	-375.9	6607.3	89.99	167.50
	86	-265.2	6667.8	91.30	168.21
	88	-154.0	6728.0	92.57	168.90
	90	-42.3	6788.3	93.83	169.56
	95	6940.0	6938.4	171.21	171.20
	100	7091.1	7088.1	172.76	172.73
5	80	-587.5	983.1	87.28	94.68
	85	-313.5	1270.8	90.60	98.18
	90	-135.6	1561.9	93.78	101.52
	96	300.9	6737.0	97.40	156.51
	100	526.4	6876.3	99.70	157.91
	104	752.9	7012.4	101.92	159.26
	108	981.0	7145.8	104.07	160.52
	110	7179.5	7211.9	160.94	161.13
	115	7349.4	7374.9	162.45	162.56
10	120	7515.3	7535.7	163.87	163.93
	100	533.9	2178.0	99.63	107.79
	104	759.8	6704.5	101.84	151.38
	106	873.2	6790.2	102.92	152.20
	108	987.1	6872.9	103.99	152.95
	110	1101.6	6953.3	105.04	153.71
	112	1216.9	7031.7	106.07	154.41
	114	1333.1	7108.5	107.10	155.08
	116	1450.5	7183.6	108.12	155.75
	118	1569.5	7257.5	109.14	156.37
20	120	7250.7	7330.7	156.55	156.99
	105	830.3	2508.0	102.23	110.59
	110	1113.5	2856.0	104.86	113.84
	115	1400.8	3249.0	107.41	117.32
	118	1576.5	6663.6	108.92	146.89
	122	1816.7	6894.7	110.92	148.72
	126	2066.4	7096.5	112.94	150.35
	130	2329.7	7280.5	115.00	151.80
	135	7312.6	7494.8	152.46	153.40
	140	7552.3	7697.1	154.21	154.89
	145	7770.4	7890.4	155.74	156.23

3. Deviations

x %mole N ₂	H ^E j/mole	S ^M j/mole °K	S ^E j/mole °K
0	0	0	0
10	36.4	2.73	.26
20	56.1	4.14	.35
30	65.7	5.09	.38
40	68.6	5.60	.37
50	66.9	5.73	.34
60	62.3	5.60	.29
70	55.2	5.09	.28
80	43.9	4.14	.24
90	26.8	2.73	.18
100	0	0	0

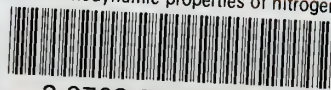
4. Summary of equimolar G^E

°K	G ^E j/mole	Fig.33 notation	Source of calculation	Source of vapor pressure data
63.14	10.88	A	7	7
65	10.76	B	1	9
70	10.28	"	"	"
77.5	9.74	"	"	"
75.16	9.65	C	5	8
77.5	10.75	D	"	5
77	10.0	E	2	2
83.82	9.2	F	6	6
90.0	9.6	G	"	10
91.0	7.3	"	"	10
80	8.45	H	This work	8
90	8.82	"	"	"
100	9.75	"	"	"
110	9.08	"	"	"
120	7.64	"	"	"

Source notation refers to "References for Excess Functions"

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The thermodynamic properties of nitrogen



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